Chapter – I

General Introduction
1.1 INTRODUCTION

Humankind since times immemorial has been generating oodles of waste, be it the bones and other parts of animals they slaughter for their food or the wood they cut to make their carts. With the rapid progress of civilization, the waste generated became of a more complex nature. At the end of the 19th century, the industrial revolution saw the rise of the world of consumers. Not only did the air get more and more polluted but the earth itself became more polluted with the generation of non-biodegradable solid waste. The immensely increase in population and rapid urbanization was also largely responsible for the increase in solid waste.

The rapid ubiquitous urbanization, immense 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. The solid waste components such as food residual, plastic and other hazardous substances have different environmental risks on heavy metal leaching. 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.

It is now known that sustainable industrial development requires the preservation of the environment. Industries create a demand not only for waste receptive services from the environmental media: air, forests, land and water but also for some material inputs supplied by the environmental resources (for example wood in the paper and pulp industry). Environmental resources can ensure a sustainable supply of these services, if they are preserved at their natural regenerative level or the demand for waste receptive services is equal to the waste assimilative capacity of environmental resources. Given that the demand for environmental services from various economic activities can exceed the natural sustainable levels of supply at a given time, and if measures are not taken to reduce
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this excess demand to zero there can be a degradation of environmental resources. The cost of reducing the demand for environmental services to the natural sustainable level of supply is regarded as the cost of sustainable use of environmental resources and in the case of industrial demand for environmental services, it is the cost of sustainable industrial development.

The environment consists of the natural capital stock of an economy, comprising of all land and natural resources, water and related biodiversity, as well as the atmosphere, which envelopes the earth. It provides the natural material inputs for the production of goods and services and nature's sink into which the wastes arising from economic activities—including production and consumption—are dumped. While a rapidly growing economy is desirable due to its beneficial social and economic effects, it also presupposes a well-functioning environment and it is now recognized that the quality of the environment and economic growth are intricately related to each other overtime. During the 1970s, and for a significant part of the 1980s, the debate on the relationship between the environment and economic growth had been largely influenced by the materials balance paradigm, which proposed strongly that economic growth, leads to a deterioration of the environment, and that an economic system can only be environmentally sustainable if it is physically in a steady state in which the amount of resources it utilizes to generate its output.

1.1.1 Types of Solid Waste

Solid waste can be classified into different types depending on their source:

- Household waste is generally classified as municipal waste
- Industrial waste as hazardous waste
- Bio-medical waste or hospital waste as infectious waste

1.1.1.1 Municipal solid waste

Consists of household waste, construction and demolition debris, sanitation residue, and waste from streets. This garbage is generated mainly from residential and commercial complexes. With rising urbanization and change in lifestyle and food habits, the amount of municipal solid waste has been increasing rapidly and its composition changing. In 1980s, cities and towns in India generated an estimated 6
million tonnes of solid waste whereas in 90s, it was about 48 million tonnes [1]. More than 25 per cent of the municipal solid waste is not collected at all and 70 per cent of the Indian cities lack adequate capacity to transport it and there are no sanitary landfills to dispose of the waste. The existing landfills are neither well equipped nor well managed and are not lined properly to protect against contamination of soil and ground water. Over the last few years, the consumer market has grown by leaps and bounds leading to products being packed in cans, aluminium foils, plastics and other such non-biodegradable items that cause incalculable harm to the environment. In India, some municipal areas have made taboo the use of plastics and they seem to have achieved success. One positive note is that in many large cities, shops have begun packing items in reusable or biodegradable bags [2].

1.1.1.2 Hazardous waste

Industrial and hospital waste is considered hazardous as they may contain toxic substances. Certain types of household waste are also hazardous. Hazardous wastes could be highly toxic to humans, animals and plants are corrosive, highly inflammable, or explosive; and react when exposed to certain things e.g. gases [3]. India generates around 15 million tonnes of hazardous wastes every year. Household wastes that can be categorized as hazardous waste include old batteries, shoe polish, paint tins, old medicines, and medicine bottles. In the industrial sector, the major generators of hazardous waste are the metal, chemical, paper, pesticide, dye, refining and rubber goods industries. Direct exposure to chemicals in hazardous waste such as mercury and cyanide can be fatal.

1.1.1.3 Hospital waste

Hospital waste is generated during the diagnosis, treatment, or immunization of human beings or animals or in research activities in these fields or in the production or testing of biological. It may include wastes like sharps, soiled waste, disposables, anatomical waste, cultures, discarded medicines, chemical wastes, etc. These are in the form of disposable syringes, swabs, bandages, body fluids, human excreta, etc.
This waste is highly infectious and can be a serious threat to human health if not managed in a scientific and discriminate manner. It has been roughly estimated that of the 4 kg of waste generated in a hospital at least 1 kg would be infected. Hospital waste contaminated by chemicals used in hospitals is considered hazardous. These chemicals include formaldehyde and phenols, which are used as disinfectants, and mercury, which is used in thermometers or equipment that measure blood pressure. Most hospitals in India do not have proper disposal facilities for these hazardous wastes. Apart from above the mentioned three categories of waste there is one more waste generated from the agriculture field called as agricultural waste or biomass. The remaining of the waste in the fields after the harvesting of the any crop is known as biomass which is also disposed into the municipal waste unused. Many developed countries have adopted the principle of the waste hierarchy in order to guide their policies on waste management. The hierarchy lays out the preferred options for managing the waste from the point where it arises through to final disposal.

1.1.2 Waste to Energy

Municipal Solid Waste (MSW) contains organic as well as inorganic matter. The latent energy present in its organic fraction can be recovered for gainful utilization through adoption of suitable Waste Processing and Treatment technologies. The recovery of energy from wastes also offers a few additional benefits as follows:

- The total quantity of waste gets reduced by nearly 60 % to over 90 %, depending upon the waste composition and the adopted technology;
- Demand for land, which is already scarce in cities, for landfilling is reduced;
- The cost of transportation of waste to far-away landfill sites also gets reduced proportionately; and
- Net reduction in environmental pollution.
Minimisation

Re-use

Recycle

Recovery

Disposal

It is, therefore, only logical that, while every effort should be made in the first place to minimize generation of waste materials and to recycle and reuse them to the extent feasible, wherever feasible, this option should be incorporated in the over-all scheme of Waste Management.

1.1.2.1 Importance of Waste to Energy

Most wastes that are generated, find their way into land and water bodies without proper treatment, causing severe water pollution. They also emit greenhouse gases like methane and carbon dioxide, and add to air pollution. Any organic waste from urban and rural areas and industries is a resource due to its ability to get degraded, resulting in energy generation. The environmental benefits of waste to energy, as an alternative to disposing of waste in landfills, are clear and compelling. Waste to energy generates clean, reliable energy from a renewable fuel source, thus reducing dependence on fossil fuels, the combustion of which is a major contributor to GHG emissions.

These measures would reduce the quantity of wastes, generate a substantial quantity of energy from them, and greatly reduce pollution of water and air, thereby offering a number of social and economic benefits that cannot easily be quantified.
1.1.2.2 India Waste to Energy Potential

According to the Ministry of New and Renewable Energy (MNRE), there exists a potential of about 1700 MW from urban waste (1500 from MSW and 225 MW from sewage) and about 1300 MW from industrial waste. The ministry is also actively promoting the generation of energy from waste, by providing subsidies and incentives for the projects. Indian Renewable Energy Development Agency (IREDA) estimates indicate that India has so far realized only about 2% of its waste-to-energy potential. A market analysis from Frost and Sullivan predicts that the Indian municipal solid waste to energy market could be growing at a compound annual growth rate of 9.7% by 2013. Any solid waste generation can be minimized on the earth the reducing, reusing, recycling the consumables used. The waste used for energy generation by different technologies like thermal conversion, thermochemical conversion, bio-chemical conversion, electrochemical conversion etc., is releasing out some gases after combustion and ash is generated after incineration which may be harmful to the human being as well as atmosphere if the proper treatment measures are taken.

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. Now-a-days, solid waste incineration plants tend to be among the most expensive solid waste management options, and they require highly and latent skilled personnel and careful maintenance [4]. Incineration is an efficient way to reduce the waste volume and demand for landfill space. In 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 °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 [5]. 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 monitoring the slag quality is immensely imperative before it is used. Most of the heavy metals in untreated ash are not soluble, but are present as insoluble.

Due to rapid industrial growth, environmental pollution has increased tremendously over the years, especially the contamination of soil and ground water with heavy metals such as chromium, lead, copper, arsenic, nickel, beryllium, antimony, zinc, magnesium, aluminum, cobalt etc. These metals, are toxic even at low concentrations, may find their way into the human body via inhalation, ingestion, and skin absorption. If accumulation of the heavy metal ions in the body tissues is faster than the body’s detoxification, a gradual buildup of these toxins will occur. Long and even short term exposure to measurable quantities of various metals such as lead, mercury, copper, nickel, arsenic, beryllium, molybdenum, zinc, chromium and antimony can lead to long term health problems and can cause irreversible damage.

According to US Environmental Protection Agency (US EPA) reports, exposure to excessive concentrations of cadmium and mercury has produced adverse health effects in public [6-7]. In addition, some of these elements may have detrimental effects upon crop growth and yield. They may also have adverse effects on ecosystem if their proper detection, analysis, disposal and dispersal are not regulated. These metals can enter into human body by contact to open lying contaminated sludge, irrigating crop with untreated waste water, chemicals,
industrial waste and effluents. The exposure to heavy metals is a serious growing problem throughout the world. The incidences of human exposure to these metals have risen dramatically in the last 10 years [8].

Keeping in view the above mentioned harmful effects of these metals, there is a need for rapid and precise determination of the concentration of contaminants, in the environment. The interest for the development of new analytical techniques has increased in the recent years to assess and monitor the extent of environmental contamination in water resources, soil, and waste disposal sites. Most of the available methods are generally expensive or time-consuming due to sample preparation, require special reagents/chemicals and are not cost effective [9-10].

1.2 HEAVY METALS

Heavy metal is a member of an ill-defined subset of elements that exhibit metallic properties, which would mainly include the transition metals, some metalloids, lanthanides, and actinides. Many different definitions have been proposed—some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity. The term heavy metal has been called a "misinterpretation" in an IUPAC technical report due to the contradictory definitions and its lack of a "coherent scientific basis". There is an alternative term toxic metal, for which no consensus of exact definition exists either. As discussed below, depending on context, heavy metal can include elements lighter than carbon and can exclude some of the heaviest metals [11] Heavy metals occur naturally in the ecosystem with large variations in concentration. In modern times, anthropogenic sources of heavy metals, i.e. pollution, have been introduced to the ecosystem [12]. Waste-derived fuels are especially prone to contain heavy metals so they should be a central concern in a consideration of their use.

There are 35 metals that concern us because of occupational or residential exposure; 23 of these are the heavy elements or "heavy metals": antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc [13]. Interestingly, small amounts of these elements are common in our environment and diet and are actually necessary for good health, but large
amounts of any of them may cause acute or chronic toxicity (poisoning). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer [14].

For some heavy metals, toxic levels can be just above the background concentrations naturally found in nature. Therefore, it is important for us to inform ourselves about the heavy metals and to take protective measures against excessive exposure. In most parts of the United States, heavy metal toxicity is an uncommon medical condition however it is a clinically significant condition when it does occur. If unrecognized or inappropriately treated, the toxicity can result in significant illness and reduced quality of life [15]. For persons who suspect that they or someone in their household might have heavy metal toxicity, testing is essential. Appropriate conventional and natural medical procedures may need to be pursued [16].

The association of symptoms indicative of acute toxicity is not difficult to recognize because the symptoms are usually severe, rapid in onset, and associated with a known exposure or ingestion [17] cramping, nausea, and vomiting; pain; sweating; headaches; difficulty breathing; impaired cognitive, motor, and language skills; mania; and convulsions. The symptoms of toxicity resulting from chronic exposure (impaired cognitive, motor, and language skills; learning difficulties; nervousness and emotional instability; and insomnia, nausea, lethargy, and feeling ill) are also easily recognized; however, they are much more difficult to associate with their cause. Symptoms of chronic exposure are very similar to symptoms of other health conditions and often develop slowly over months or even years.
1.2.1 Occurrence of Heavy Metals in Environment

"Heavy metals" are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 4°C (39°F). Simply stated, specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well-known toxic metallic elements with a specific gravity that is 5 or more times that of water are arsenic, 5.7; cadmium, 8.65; iron, 7.9; lead, 11.34 and mercury, 13.546 [18]. In small quantities, certain heavy metals are nutritionally essential for a healthy life. Some of these are referred to as the trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products [19]. Diagnostic medical applications include direct injection of gallium during radiological procedures, dosing with chromium in parental nutrition mixtures and the use of lead as a radiation shield around x-ray equipment [20]. Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, and so forth [21]. Many of these products are in our homes and add to our quality of life when properly used.

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies in routine food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain [22]. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers and groundwater [23].
1.2.2 Sources of Heavy Metals

Heavy metals are derived from various sources and the sources are varied from space and time. The general occurrence of heavy metals is waste of mining industrial and agriculture products.

1.2.2.1 Waste

Heavy metals entering the technosphere will sooner or later be discharged to the environment or end up in waste. Heavy metals may end up in solid waste during all life cycle phases of the products as illustrated in the figure below. The term ‘the technosphere’ will be applied here, and should be considered equal to other terms like ‘the economy’, ‘the physical economy’ or ‘the Society’[24]. The figure below shows the overall flows, in practice each step on the figure may consist of several minor steps.

![Diagram of the flow of heavy metals](image_url)

**Fig 1.2 Schematic illustration of the overall flow of heavy metals to waste**

* Tailing and other mining waste
1.2.2.2 Mining and Extraction

By mining and extraction a part of the heavy metals will end up in tailings and other waste products. Waste from mining and processing is not specifically addressed in the present work. A significant part of the turnover of the four heavy metals with mining waste actually concerns the presence of the heavy metals in waste from extraction of other metals like zinc, copper and nickel. It should, however, be kept in mind that mining waste is generated independent of the subsequent application of the heavy metal [25].

1.2.2.3 Agriculture fields

Heavy metals are introduced into the environment either by natural means or by anthropogenic activities. In nature excessive levels of trace metals may occur by geographical phenomena like volcanic eruptions, weathering of rocks and their leaching into rivers, lakes and oceans due to action of wind are major anthropogenic sources [26]. Certain amount of heavy metals are released while mining and uncontrolled smelting of large quantities of metals ore in open fires. The industrial renovation, metals extraction from natural resources and processing in industries are sources from where the heavy metals leak into atmosphere [27]. Similarly trace heavy metals are deposited in the environment through discharge of waste both from domestic, agriculture and from auto exhausts.

1.2.2.4 Heavy Metals Reaching the Ecosystem

Many toxic organic compounds and heavy metals from different sources are deposited and buried in the soil or water. They also reach water bodies when transported by running water from soil [28]. Humus and organic material present in the soil have high affinity for heavy metal cations and extracts them from water that passes through soil. Roots of crops and other plants pick up these compounds along with water. Heavy metals are also retained in the soil by adsorption on mineral particles of the soil and precipitation reactions [29].

1.2.2.5 Heavy Metal Existence in Agriculture Soil

Trace elements are introduced into soils from various sources, including atmospheric deposition of metal/metalloid-bearing particles, application of sewage sludge, phosphate fertiliser, pig slurry and pesticides, where they exist in several
chemical forms. Their fate in soil depends on the chemical state of the element in the contaminating material. Plants are essential components of natural ecosystems and agro-ecosystems, and are the first compartment of the terrestrial food chain. When grown on polluted soils they become a potential threat to human and animal health, as they may accumulate toxic elements (e.g. metals) in their tissues, as dramatically illustrated by the Itai-Itai disease that affected farmers on a long-term diet of cadmium-contaminated rice. Plants may also have their growth sharply reduced by high levels of toxic elements in their tissues, causing a decrease in crop yields and further economic damage to farmers, as can be observed near metal smelters or mine spoils. On the other hand, some elements, toxic when present at high concentration in tissues, are also essential to plants, and their deficiency induces loss in biomass production and physiological disorders in plants.

Application of agricultural products to soil and crops became a common practice in horticulture. The major objectives of this practice are increasing the supplying of the nutrients (fertilizers), correction of soil pH and protection of crops from pest, although, these practices can promote the soil degradation as result from elements and compounds uptake to undesirable levels [30].

Contaminated soils have a direct impact on animal and human health through the quality of food and water [31]. In this way the cultivated agricultural areas are, on the basis of land area, potentially large contributors of nonpoint sources leading to environmental pollution in aquatic systems. These soils have been estimated to be responsible for 95 - 99% of soil erosion [32]. The sediment resulting from this process is today recognized as being the largest single pollutant affecting water quality. Not only is the storage capacity of manmade impoundment reduced by silting, agricultural runoff provides sufficient nutrients to cause excessive algae growth [33].

In contrast to being eroded, soil may become enriched with hazardous heavy metals by the application of plant nutrients and crop protective measures. Conventional inorganic phosphorous fertilizers may cause an inadvertent addition of heavy metals, which are contained as impurities like chromium, cadmium, copper, zinc, nickel and lead [34]. Phosphate rock can induce high concentrations of Cd,
Zn, Cr, Cu and Pb in diammonium phosphate. The work investigated the distribution of heavy metals in tomato, sweet pepper and pineapple soils cultivated in north of Rio de Janeiro state, Brazil.

Apart from pH, other soil properties, such as cation exchange capacity (CEC), organic matter content, quantity and type of clay minerals, the content of the oxides of iron (Fe), aluminum (Al), and manganese (Mn), and the redox potential determine the soil’s ability to retain and immobilize heavy metals. When this ability is exceeded, the quantities of heavy metals available to plants increase, resulting in the appearance of toxicity phenomena.

In soil science, cation exchange capacity (CEC) is the capacity of a soil for ion exchange of cations between the soil and the soil solution. CEC is used as a measure of fertility, nutrient retention capacity, and the capacity to protect groundwater from cation contamination. Cations can also be easier to understand by just adding the group number.

The quantity of positively charged ions (cations) that a clay mineral or similar material can accommodate on its negatively charged surface is expressed as milli-ion equivalent per 100 g, or more commonly as milliequivalent (meq) per 100 g or cmol/kg. Clays are aluminosilicates in which some of the aluminium and silicon ions have been replaced by elements with different valence, or charge. For example, aluminium (Al$^{3+}$) may be replaced by iron (Fe$^{2+}$) or magnesium (Mg$^{2+}$), leading to a net negative charge. This charge attracts cations when the clay is immersed in an electrolyte such as salty water and causes an electrical double layer. The cation-exchange capacity is often expressed in terms of its contribution per unit pore volume, $Q_c$.

![Fig.1.3 Heavy metals in soil particle](image.png)
Heavy metals tend to form complexes with organic matter in the soil (humic and fulvic acids), which are different for each metal. Organic matter plays an important role not only in forming complexes, but also in retaining heavy metals in an exchangeable form. These two properties affect each heavy metal differently. For example, Cu is bound and rendered unavailable chiefly through the formation of complexes, while Cd is retained in an exchangeable form and is more readily available.

The CEC of a soil depends upon its organic matter content and clay type and content. In general the higher the CEC, the greater will be the ability to retain heavy metals. The type and quantity of clay determines the CEC, which increases with clay content, particularly when it contains a high proportion of 2:1 lattice-type minerals (e.g., montmorillonite). The specific soil surface is also closely related to clay content and type. [35] reported that the soil’s ability to retain heavy metals is more closely tied to the specific surface than to the soil CEC.

In cases of soil pollution by heavy metals, it is important to identify the available and unavailable forms of the heavy metals to ensure that the soil is managed in such a way as to prevent the unavailable forms from becoming available. The most common and simple way to identify the forms in which heavy metals are found in soils is to use sequential extraction in which components loosely held by the soil are extracted first, followed by those more tightly bonded [36].

1.3 IMPACTS OF HEAVY METALS ON ENVIRONMENT AND HUMAN

1.3.1 Environmental and health risks

The effects of the heavy metals in the environment are Lead, Cadmium, and Mercury etc are presented below

1.3.1.1 Arsenic

Arsenic is found in the natural environment in some abundance in the Earth’s crust and in small quantities in rock, soil, water and air. It is present in different minerals. About one third of the arsenic in the atmosphere comes from natural
sources, such as volcanoes, and the rest comes from man-made sources. Due to natural geological contamination, high levels of arsenic can be found in drinking water that has come from deep drilled wells. Arsenic in weathered rock or soil can be picked up and moved by the wind and water. Many arsenic compounds bind to soil and only move short distances when water percolates down through the soil. If arsenic is released into the atmosphere by industrial processes or volcanic activity, it attaches to particles that are dispersed by the wind and fall back to the ground. Microbes in soil and sediment also release substances containing arsenic into the atmosphere [37]. These are then converted to other arsenic compounds that settle back onto the ground. Arsenic is a poisonous substance, which is released both from certain human activities and naturally from the Earth's crust. Humans may be exposed to arsenic mainly through food and water, Agricultural products through soil, particularly in certain areas where the groundwater & soil is in contact with arsenic-containing minerals. Industrial processes such as mining, smelting and coal-fired power plants all contribute to the presence of arsenic in air, water and soil. Environmental contamination also occurs because it is used in agricultural pesticides and in chemicals for timber preservation.

1.3.1.2 Cadmium

Cadmium derives its toxicological properties from its chemical similarity to zinc an essential micronutrient for plants, animals and humans. Cadmium is biopersistant and, once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted [38]. In humans, long-term exposure is associated with renal disfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer, although data concerning the latter are difficult to interpret due to compounding factors. Cadmium may also produce bone defects (osteomalacia, osteoporosis) in humans and animals. In addition, the metal can be linked to increased blood pressure and effects on the myocardium in animals, although most human data do not support these findings. The average daily intake for humans is estimated as 0.15µg from air and 1µg from water. Smoking a packet of 20 cigarettes can lead to the inhalation of around 2-4µg of cadmium, but levels may vary widely.
1.3.1.3 Chromium

Chromium is used in metal alloys and pigments for paints, cement, paper, rubber and other materials. Low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage too circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium.

People can be exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium(IV); hexavalent chromium. For most people eating food that contains chromium (III) is the main route of chromium uptake, as chromium (III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the chromium contents of food. When food is stored in steel tanks or cans chromium concentrations may raise.

- Skin rashes
- Upset stomachs and ulcers
- Respiratory problems
- Weakened immune systems
- Kidney and liver damage
- Alteration of genetic material
- Lung cancer
- Death

The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath and nasal itch.
1.3.1.4 Copper

Copper can be found in many kinds of food, in drinking water and in air. Because of that we absorb enormous quantities of copper each day by eating, drinking and breathing. The absorption of copper is necessary, because copper is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of copper, too much copper can still cause health hazards. Copper concentrations in air are usually quite low, so that exposure to copper through breathing is negligible. But people who live near smelters that process copper ore into metal do experience this kind of exposure.

People who live in houses that still have copper plumbing are exposed to higher levels of copper than most people, because copper is released into their drinking water through corrosion of pipes. Occupational exposure to copper often occurs. In the work place environment, copper contangion can lead to a flu-like condition known as metal fever. This condition will pass after two days and is caused by over sensitivity. Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhoea. Intentionally high uptakes of copper may cause liver and kidney damage and even death. Whether copper is carcinogenic has not been determined yet.

There are scientific articles that indicate a link between long-term exposure to high concentrations of copper and a decline in intelligence with young adolescents. Whether this should be of prime concern is a topic for further investigation. Industrial exposure to copper fumes, dusts or mists may result in metal fume fever with atrophic changes in nasal mucous membranes. Chronic copper results in Wilson’s disease, characterized by a hepatic cirrhosis, brain damage, demyelization, renal disease and copper deposition in the cornea.

1.3.1.5 Cobalt

Cobalt is an element that occurs naturally in many different chemical forms throughout environment. Small amounts of cobalt are essential for good health. It is a natural earth element and is present in trace amounts in soil, plants and in human diets. In pure form it is a steel-grey to black shiny hard metal. It also exists as Cobalt
II and Cobalt III, which form a number of organic and inorganic salts. Cobalt usually occurs in association with other metals such as copper, nickel, manganese and arsenic. Small amounts are found in most rocks, soil, surface and underground water, plants and animals. Natural sources of cobalt in the environment are soil, dust, seawater, volcanic eruptions and forest fires. It is also released to the environment from burning of coal and oil, from car, truck and airplane exhausts and from industrial processes that use the metal or its compounds. Cobalt and its salts are used in a variety of processes — to make super alloys which maintain their strength at high temperatures; as paint drier; as a ground coat for porcelain enameling used on steel bathroom fixtures and large appliances; and as an ingredient of coloured pigments. Cobalt is essential in trace amounts for human life. It is part of vitamin B-12, and plays a key role in the body’s synthesis of this essential vitamin. Cobalt has also been used as a treatment for anemia, because it causes red blood cells to be produced. The toxicity of cobalt is quite low compared to many other metals in soil.

1.3.1.6 Lead

In humans exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing infant being more sensitive than the adult. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system and acute or chronic damage to the nervous system. Lead poisoning, which is so severe as to cause evident illness, is now very rare indeed. At intermediate concentrations, however, there is ample persuasive evidence that lead can have small, subtle, subclinical effects, particularly on neuropsychological developments in children. Some studies suggest that there may be a loss of up to 2 IQ points for a rise in blood lead levels from 10 to 20µg/dl in young children.

Most people receive the bulk of their lead intake from food, in specific populations other sources may be more important, such as water in areas with lead piping, air near point of source emissions, soil, dust, paint flakes in old houses or contaminated land. Lead in the air contributes to lead levels in food through
deposition of dust and rain containing the metal, on crops and the soil. For the majority of people however, dietary lead exposure is well below the provisional tolerable weekly intake recommended by World Health Organization [39].

1.3.1.7 Mercury

Mercury is a toxic substance which has no known function in human biochemistry or physiology and does not occur naturally in living organisms. Inorganic mercury poisoning is associated with tremors, gingivitis and/or minor psychological changes, together with spontaneous abortion and congenital malformation. Mono-methyl-mercury causes damage to the brain and the central nervous system, while foetal and postnatal exposure have given rise to abortion, congenital malformation and development changes in young children.

1.3.1.8 Nickel

Nickel is a compound that occurs in the environment only at very low levels. Humans use nickel for many different applications. The most common application of nickel is the use as an ingredient of steal and other metal products. It can be found in common metal products such as jewellery. Odd stuffs naturally contain small amounts of nickel. Chocolate and fats are known to contain severely high quantities. Nickel uptake will boost when people eat large quantities of vegetables from polluted soils. Plants are known to accumulate nickel and as a result the nickel uptake from vegetables will be eminent. Smokers have a higher nickel uptake through their lungs. Finally, nickel can be found in detergents.

Humans may be exposed to nickel by breathing air, drinking water, eating food or smoking cigarettes. Skin contact with nickel-contaminated soil or water may also result in nickel exposure. In small quantities nickel is essential, but when the uptake is too high it can be a danger to human health.

An uptake of too large quantities of nickel has the following consequences:

- Higher chances of development of lung cancer, nose cancer, larynx cancer and prostate cancer
- Sickness and dizziness after exposure to nickel gas
- Lung embolism
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General Introduction

- Respiratory failure
- Birth defects
- Asthma and chronic bronchitis
- Allergic reactions such as skin rashes, mainly from jewellery,
- Heart disorders

Nickel fumes are respiratory irritants and may cause pneumonitis. Exposure to nickel and its compounds may result in the development of a dermatitis known as “nickel itch” in sensitized individuals. The first symptom is usually itching, which occurs up to 7 days before skin eruption occurs. The primary skin eruption is erythematous, or follicular, which may be followed by skin ulceration. Nickel sensitivity, once acquired, appears to persist indefinitely. Small amounts of Nickel are needed by the human body to produce red blood cells, however, in excessive amounts, can become mildly toxic. Short-term overexposure to nickel is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation. The EPA does not currently regulate nickel levels in drinking water. Nickel can accumulate in aquatic life, but its presence is not magnified along food chains.

1.3.1.9 Manganese

Manganese is a very common compound that can be found everywhere on earth. Manganese is one out of three toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic when too high concentrations are present in a human body. When people do not live up to the recommended daily allowances their health will decrease. But when the uptake is too high health problems will also occur.

The uptake of manganese by humans mainly takes place through food, such as spinach, tea and herbs. The foodstuffs that contain the highest concentrations are grains and rice, soya beans, eggs, nuts, olive oil, green beans and oysters. After absorption in the human body manganese will be transported through the blood to the liver, the kidneys, the pancreas and the endocrine glands. Manganese effects occur mainly in the respiratory tract and in the brains. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage. Manganese can also
cause Parkinson, lung embolism and bronchitis. When men are exposed to manganese for a longer period of time they may become impotent. A syndrome that is caused by manganese has symptoms such as schizophrenia, dullness, weak muscles, headaches and insomnia.

Because manganese is an essential element for human health shortages of manganese can also cause health effects. These are the following effects:

- Fatness
- Glucose intolerance
- Blood clotting
- Skin problems
- Lowered cholesterol levels
- Skeleton disorders
- Birth defects
- Changes of hair colour
- Neurological symptoms

Chronic Manganese poisoning may result from prolonged inhalation of dust and fume. The central nervous system is the chief site of damage from the disease, which may result in permanent disability. Symptoms include languor, sleepiness, weakness, emotional disturbances, spastic gait, recurring leg cramps and paralysis. A high incidence of pneumonia and other upper respiratory infections has been found in workers exposed to dust or fume of Manganese compounds. Manganese compounds are experimental equivocal tumorigenic agents.

1.4 TECHNOLOGIES TO CONVERT WASTE TO ENERGY

The term “waste to energy” has traditionally referred to the practice of incineration of garbage. Today, a new generation of waste-to-energy technologies is emerging which hold the potential to create renewable energy from waste matter, including municipal solid waste, industrial waste, agricultural waste and waste by-products. The main categories of waste-to-energy technologies are physical technologies, which process waste to make it more useful as fuel; thermal technologies, which can yield heat, fuel oil, or syngas from both organic
and inorganic wastes and biological technologies in which bacterial fermentation is used to digest organic wastes to yield fuel [40].

Waste-to-energy technologies convert waste matter into various forms of fuel that can be supply energy. Waste feedstocks can include municipal solid waste (MSW); construction and demolition (C&D) debris; agriculture waste such as crop silage and livestock manure; industrial waste from coal mining, lumber mills or other facilities; and even the gases that are naturally produced within landfills. Energy can be derived from waste that has been treated and pressed into solid fuel, waste that has been converted into biogas or syngas or heat and steam from waste that has been incinerated. Waste-to-energy technologies that produce fuel are referred to as waste-to-fuel technologies. Advanced waste-to-energy technologies can be used as to produce biogas (methane and carbon dioxide), syngas (hydrogen and carbon monoxide), liquid biofuels (ethanol and biodiesel), or pure hydrogen and these fuels can then be converted into electricity. The primary categories of technology used for waste-to-energy conversion are physical methods thermal methods and biological methods.

Technological Tree

```
Waste to Energy  →  Physical  →  Refuse Derived Fluff
      Thermal                         →  Combustion
                           →  Pyrolysis
                               →  Thermal gasification
                                                                →  Plasma-arc gasification
                                      Biological  →  Fermentation
                                                               →  Methane capture/landfill gas
```

Fig. 1.4 Technological tree
1.4.1 Physical Technology

Physical waste-to-energy technologies mechanically process waste to produce forms more suitable for use as fuel, producing refuse-derived fuel (RDF) or solid recovered fuel (SRF). RDF is a fuel produced by either shredding solid waste (such as MSW, C&D debris or sludge) or treating it with steam pressure in an autoclave. RDF consists largely of organic materials taken from solid waste streams, such as plastics and biodegradable waste. The municipal waste is first processed to remove glass, metals and other materials that are not combustible (many of which can then be recycled). Autoclaving (treating with high-pressure steam) kills viruses and other potential pathogens and it also causes plastics to soften and flatten, paper and other fibrous material to disintegrate and bottles and metal objects to be cleaned of labels. This process reduces the volume of the waste by up to 60% and the residual material can then be compressed into pellets or bricks and sold as solid fuel. Burning RDF is more clean and efficient than incinerating MSW or other solid waste directly but the processing adds to costs.

![Fig 3. Physical process of conversion waste](image-url)
1.4.2 Thermal Technology

Thermal waste-to-energy technologies use heat or combustion to treat wastes. The thermal methods include the following:

1.4.2.1 Combustion Technology

Municipal waste can be directly combusted in waste-to-energy incinerators as a fuel with minimal processing in a process known as "mass burn". Heat from the combustion process is used to turn water into steam, which is used to power a steam-turbine generator to produce electricity. Next-pollutants captured in this process must still be disposed of.

1.4.2.2 Pyrolysis and thermal gasification

Pyrolysis uses heat to break down organic materials in the absence of oxygen, producing a mixture of combustible gases (primarily methane, complex hydrocarbons, hydrogen and carbon monoxide), liquids and solid residues. Low-temperature paralysis can also be used to produce a synthetic diesel fuel from waste-film plastic, for example a beneficial by product of pyrolysis is a kind of charcoal called "biochar", which can be used as a fertilizer and can also be used to absorb CO₂ and other emissions from coal-fired power plants. Thermal gasification of waste, in contrast to pyrolysis, takes place in the presence of limited amount of oxygen. The gas generated by either of these processes can be used in boilers to provide heat or it can be cleaned up and used in combustion turbine generators. Whereas incinerations convert the input waste into energy onsite, pyrolysis and thermal gasification allow the production of fuel that can be transported. In addition, the gases, oils and solid char from pyrolysis and gasification can also be purified and used as a feedstock for chemical production and for other applications.

1.4.2.3 Plasma-arc gasification

Plasma-arc waste-to-fuel gasification uses a plasma-arc torch to produce temperatures as high as 13,000 °F. This extreme heat breaks down wastes, forming syngas (hydrogen and carbon monoxide) and a rock-like solid by-product called slag, which can be used in construction or road asphalt. As in coal gasification, the syngas can be converted into a variety of marketable fuels – including ethanol, natural gas (methane), and hydrogen – or it can be used to generate electricity.
directly. Plasma converters could consume nearly any type of waste, including concrete, steel and toxic chemicals, but the technology requires large energy inputs.

1.4.3 Biological Technology

Biological waste-to-energy technologies are those that use microbes or other organisms to produce fuel from waste. Varieties include the following:

1.4.3.1 Methane capture/landfill gas

Landfilling is still the primary method of disposal of municipal solid waste and C & D debris in the U.S. and many other countries. If left undisturbed, landfill waste produces significant amounts of gaseous by-products, consisting mainly of carbon dioxide (CO₂) and methane (natural gas, CH₄). This “landfill gas” or “biogas” is produced by anaerobic (oxygen-free) digestion of organic matter. Carbon dioxide and methane are both greenhouse gases that increase the risk of climate change when they are released unimpeded into the atmosphere, but methane is also a useful source of energy and therefore worth collecting as biogas. Landfill gas can be captured via a collection system, which usually consists of a series of well drilled into the landfill and connected by a plastic piping system. The gas can then be burned directly in a boiler as a heat energy source or if the biogas is cleaned by removing water vapour and sulphur dioxide, it can be used directly in internal-combustion engines or for electricity generation via gas turbines or fuel cells.

1.4.3.2 Biogas plants

Anaerobic digestion to produce biogas can occur either naturally (as in landfill gas) or in a controlled environment like a biogas plant. Feed stocks in such plants could include food-processing waste or other agricultural waste such as manure. The process begins with placement of waste and various types of bacteria into an airtight container called a digester. Advances digester systems can now produce biogas with pure methane content higher than 95%. The biogas can then either be burned directly in boilers or cleaned and supplied as natural gas. Biogas plants can transfer electrical energy to the main utility grid or they can generate power for use on-site in applications like lighting, processing plants, ethanol plant and greenhouses. Biogas plant has been deployed in India, Israel, Australia etc.
1.4.3.3 Fermentation

Fermentation uses yeast to generate liquid ethanol from biomass waste.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste reduction</td>
<td>• Low-tech, low-cost</td>
<td>• Requires change in behaviour</td>
</tr>
<tr>
<td></td>
<td>• Reduces amount of waste that must be dealt with in any fashion</td>
<td>• Doesn’t produce energy</td>
</tr>
<tr>
<td>Recycling</td>
<td>• Reduces waste without need for incineration or other more advanced methods</td>
<td>• Requires change in behaviour</td>
</tr>
<tr>
<td></td>
<td>• Doesn’t produce energy</td>
<td>• Doesn’t produce energy</td>
</tr>
<tr>
<td></td>
<td>• Consumes energy</td>
<td></td>
</tr>
<tr>
<td>Composting</td>
<td>• Reduces waste without need for incineration</td>
<td>• Requires change in behaviour</td>
</tr>
<tr>
<td></td>
<td>• Produces fertilizers</td>
<td>• Doesn’t produce energy</td>
</tr>
<tr>
<td>Landfill dumping</td>
<td>• Quick, easy disposal of waste</td>
<td>• Uses potentially valuable land</td>
</tr>
<tr>
<td></td>
<td>• Doesn’t involve incineration</td>
<td>• Doesn’t produce energy</td>
</tr>
<tr>
<td></td>
<td>• Can leach toxins into groundwater</td>
<td>• Releases significant greenhouse-gas emissions, especially methane</td>
</tr>
<tr>
<td>Solar power</td>
<td>• Free beyond initial capital investment and maintenance</td>
<td>• Efficiency of only 6% to 20%</td>
</tr>
<tr>
<td></td>
<td>• More consistent supply of power than some other renewable sources</td>
<td>• Requires consistent minimum levels of sunlight; not suitable for cloudy climates or useful after sundown</td>
</tr>
<tr>
<td></td>
<td>• Available to many regions</td>
<td></td>
</tr>
<tr>
<td>Tidal energy</td>
<td>• Zero emissions</td>
<td>• High maintenance costs</td>
</tr>
<tr>
<td></td>
<td>• Can produce more power per turbine than wind</td>
<td>• Requires proximity to coast or river</td>
</tr>
<tr>
<td></td>
<td>• Somewhat intermittent: power not generated at slack tide</td>
<td>• Somewhat intermittent: power not generated at slack tide</td>
</tr>
<tr>
<td></td>
<td>• Still in early R&amp;D phase</td>
<td>• Still in early R&amp;D phase</td>
</tr>
<tr>
<td>Hydroelectric power</td>
<td>• Low-cost energy generation</td>
<td>• Dam construction can destroy habitats and alter local ecosystems</td>
</tr>
<tr>
<td></td>
<td>• Renewable non-polluting resource</td>
<td>• Must be located on significant waterway; not suitable for drier regions</td>
</tr>
<tr>
<td></td>
<td>• Creates new reservoirs or lakes</td>
<td></td>
</tr>
<tr>
<td>Wind power</td>
<td>• Free beyond initial capital investment and maintenance</td>
<td>• Efficiency of only 20% to 30% for ground-based systems</td>
</tr>
<tr>
<td></td>
<td>• Already cost-competitive with fossil fuels</td>
<td>• High initial capital cost intermittent power production</td>
</tr>
<tr>
<td></td>
<td>• Can supply localized power independent of grid</td>
<td></td>
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<tr>
<td></td>
<td>• Relatively small footprint</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Zero emissions</td>
<td></td>
</tr>
<tr>
<td>Nuclear power</td>
<td>• Well-established and cost-competitive with the least expensive energy sources used today</td>
<td>• Radioactive waste from power plants takes hundreds to thousands of years to decay, and therefore must be stored in a safe long-term location</td>
</tr>
<tr>
<td></td>
<td>• Lower emissions – i.e., pollutants and greenhouse gases – than coal and other conventional power</td>
<td>• Risk of &quot;melt down&quot; or Chernobyl-scale disasters</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Capital costs to build safe plants are large</td>
</tr>
</tbody>
</table>
1.4.4 Technology drivers

1.4.4.1 Improved pollution and emissions controls for combustion

One of the primary objections against waste incineration, even when used to generate energy has been that burning releases particulate matter and pollutants like nitrogen oxides (NOx) into the atmosphere. However improved technologies for treating gas waste streams are mitigating these concerns.

1.4.4.2 Advanced non-incineration conversion methods

New technologies like pyrolysis thermal gasification and plasma-arc gasification are providing ways of generating energy from waste that avoid many of the pollution concerns around incineration and may provide better economics for waste-to-energy as well.

1.4.4.3 Hydrogen production enabling other clean technologies like fuel cells

Waste-to-energy systems like thermal gasification-based waste conversion plants can be fitted with direct hydrogen generation. While many countries are interested in developing a hydrogen infrastructure for fuel-cell-powered vehicles, in most cases including the U.S. and Canada, current plans include only hydrogen generation from coal plant. Waste-to-energy system could provide a more sustainable solution.

1.4.5 Strategic drivers

1.4.5.1 Reduction in landfill dumping

Landfills require large amount of land that could be used for other purposes. Municipalities that run out of space for landfills must pay to have their garbage and construction debris shipped somewhere else. For example, Toronto pays to have almost 8,00,000 tons per year of its excess gaebage shipped to Michigan, at $22 per ton. New York city pays up to $120 per ton to ship its solid waste landfills. Converting municipal waste to energy reduces the volume of ordinary solid waste bound for landfills by up to 90% and by producing useful products can help cut costs further.
1.4.5.2 Reduced dependence on fossil fuels

With advanced technologies, waste can be used to generate fuel that does not require mining or drilling for increasingly scarce and expensive non-renewable fossil-fuel resources.

1.4.5.3 Reduced greenhouse-gas emissions and pollution

Using waste as a feedstock for energy production reduces the pollution caused by burning coal or other fossil fuels. While traditional incineration still produces CO2 and pollutants, advance methods such as gasification have the potential to provide a double benefit reduced CO2 emissions compared with incineration or coal plants and reduced methane emissions from landfills.

1.4.5.4 Eligibility for carbon credits and tax incentives

Because they replace fossil-fuel use, most advanced waste to energy technologies is eligible for greenhouse-gas emission credits. These credits can be used by corporations to offset greenhouse gas emissions or sold as a commodity via carbon cap-and-trade programs like the Chicago climate exchange. In addition, government programs in several EU countries are promoting the use of biogas from waste and offering tax incentives for producers.

1.5 ANALYTICAL INSTRUMENTATION TECHNIQUES

1.5.1 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES)

It has long been known that distinctive colours are produced when compounds of certain metals are vaporized in flames. In a common high school experiment, salts of sodium produce a yellow light in the flame of a Bunsen burner, calcium salts colour the flame brick-red, barium salts green and so on. It was shown in the last century that the optical spectra of these collared flames contain lines or bands at wavelengths characteristic of the particular elements.

With the development of quantum mechanics in the early part of the twentieth century, the lines and bands were shown to arise from electronic transitions in specific atoms or molecules. The yellow sodium flame, for example, results from a pair of lines at 588.995 nm and 589.592 nm, emitted by sodium atoms, while the characteristic colours of the calcium and barium flames arise.
principally from molecular emission bands of the monohydroxides. In the 1860s, Bunsen and Kirchhoff established flame spectroscopy as a highly sensitive and specific means of identifying minute quantities of certain elements. Bunsen discovered rubidium and caesium in German mineral waters after observing lines in the flame spectra that could not be attributed to any known element. Several other new elements were discovered following observations of their characteristic spectral lines. Perhaps the most noteworthy of these was helium, whose existence was postulated in 1868 to account for an unidentified line in the spectrum of the sun, some twenty-seven years before the element was finally detected on the earth in gases from a uranium mineral. From these promising beginnings, optical emission spectrometry developed into a powerful method of chemical analysis, in which the concentration of a specific element in a sample is related to the intensity of lines in its optical spectrum.

Flame emission spectrometry, for example, was developed by Lundegardh and others in the 1930s as a series of refinements of the flame spectroscopic methods used by Kirchhoff and Bunsen and their successors in the late nineteenth century. The sample solution is introduced into the flame as a fine spray, generated at a uniform and reproducible rate. The intensities of the characteristic spectral lines of the elements of interest are then measured with a filter spectrometer or simple monochromatic with electronic detection and readout. Flame spectrometry has been very widely used for the determination of sodium, potassium and several other elements by measuring the intensity of light emitted at a wavelength characteristic of an analyze element when samples are sprayed into the flame. The relationship between light intensity and analyze concentration is established by measuring the light emission when calibrating solutions of known concentration (often, though inaccurately called 'standards') are sprayed into the flame.

1.5.1.1 The main steps in analyzing samples by ICP-AES may be stated quite simply
1. The elements to be determined are selected.
2. Solutions of the samples are prepared, using the conventional techniques of quantitative chemical analysis.
3. 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.

4. The calibrating solutions and sample solutions are sprayed into the plasma and the intensities of appropriate emission lines are recorded.

5. Calibration graphs ('analytical working curves') are prepared for each element from the emission intensities of the calibrating solutions.

6. 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.

7. Concentrations of the elements in the sample solution and the known dilution factor.

8. 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.

1.5.1.2 Historical background of ICP-AES

A plasma is simply a gas whose properties are influenced by the presence of a significant, if often rather small, concentration of ions and electrons. These exist in approximately equal numbers over the volume of the plasma, so overall electrical neutrality is maintained. The generation of plasmas by inductive heating of gases at reduced pressure was first explored by [41] and subsequently by [42].

They experimented with atmospheric pressure radio frequency (RF) inductively coupled plasmas (ICP) with a view to industrial applications. The first major application of an ICP was reported in 1961 by Reed who used it to grow crystals of refractory (high melting point) compounds such as alumina. He found that refractory powders introduced into the central axis of the ICP were completely vaporised. Reed's ICP was similar to those used in modern spectrochemical analysis. Following the publication of Reed's work, Greenfield and his associates in Britain and Wendt and Fussel, in the USA independently developed ICP systems for spectrochemical analysis.
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Greenfield, like Reed, used a torch consisting of three concentric quartz tubes with the innermost tube being used for injecting sample material directly into the hot core of the plasma. The spectrometer was set up to view light emitted from the somewhat cooler ‘tail flame’, downstream from the ‘fireball’ of the plasma. This allowed measurements of analytical lines to be made against a relatively low-intensity background.

The emitting analyte atoms in the tail flame were located in an optically-thin central channel, which favoured the collection of emitted light by the spectrometer and promoted a linear relationship between light intensity and analyte concentration over a wide range of concentrations. The crucial importance of injecting sample material directly into the plasma along its central axis was not at first realized by other workers.

In Wendt and Fassel’s system, sample was swept around the plasma rather than through a central channel. Veillon and Margoshes found severe inter-element effects and poor detection limits with this arrangement. Later, Fassel’s group developed an ICP torch that permitted the injection of sample aerosol into a central channel through the plasma and in 1969 Dickinson and Fassel reported detection limits in the range 10-2 - 10-3 mg/L for many elements - at least one hundred times better than had been achieved previously.

Commercial ICP-AES instruments using the relatively low-power ICP torches developed by Fassel’s group became available in 1974 and since then ICP-AES has become increasingly well established in laboratories the world over. The technique is now recognized by authorities such as the United States Environmental Protection Agency (USEPA) as an approved method for many trace elements determination.
Instrumentation for ICP-AES

Figure-2.7 Emission Energy diagram

1.5.1.3 Overview of ICP-AES

A typical arrangement for ICP-AES is shown above and consists of:

1. A sample introduction system
2. The ICP torch and its associated gas supplies
3. A radio-frequency generator
4. An optical spectrometer
5. Detectors and associated electronics
6. Computerized instrument control, data collection and analysis.
1.5.1.3.1 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.

1.5.1.3.2 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.

1.5.1.3.3 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 generators 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.

1.5.1.3.4 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.

1.5.1.3.5 Detector and Readout System

At present, 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 interest in applying the new generation of solid state optical detectors in ICP-AES.
1.5.1.4 Comparison of ICP-AES and Flame-AAS

1.5.1.4.1 Detection limits

The detection limit is the concentration of analyte corresponding to the smallest signal that can be distinguished from random fluctuations in the background according to a statistical measure of significance. The detection limits with ICP-AES generally lie in the range 10⁻¹⁰ - 10⁻⁴ mg/L, and for the vast majority of elements are from 1 to 50 times better than with flame-AAS. They are better still for elements such as B, Ge, Hf, Nb, Re, Ta, Th, U, W, Zr and most of the lanthanides.

Flame-AAS determination of these elements is limited by the formation of refractory oxides or carbides that resist dissociation to free atoms. This problem is largely overcome in the ICP by the much higher temperature and the inert argon environment. On the other hand, flame-AAS shows better limits of detection than does ICP-AES for the alkali metals. This is because the alkali metals are almost completely ionized in the ICP, the resulting ions having extremely stable electronic configurations and consequently not producing intense emission spectra at ICP temperatures.
Detection limits for many of the first-row transition metals (Co, Cr, Cu, Fe, Mn and Ni) and also for Ag, Au, Bi, Ga, In, Mg, Pb, Sb, Te and Tl) are similar for both techniques. Apart from the alkali metals, those elements which can be determined by flame-AAS in an air-acetylene flame show similar detection limits in flame-AAS and ICP-AES. Those elements whose determination by flame-AAS requires the nitrous oxide/acetylene flame have much better detection limits by ICP-AES than by flame-AAS.

Above all ICP-AES is suitable for the determination of at least 72 elements. The non-metals I, P and S are best determined at wavelengths requiring a vacuum-ultraviolet spectrometer. The alkali metals, particularly Rb and Cs, are better determined by either flame-AAS or flame-AES than by ICP-AES.

1.5.1.5 Comparison of ICP-AES with graphite furnace-AAS

Graphite furnace-AAS (GF-AAS) provides excellent detection limits, up to 100-1000 times better than either ICP-AES or flame-AAS). Unfortunately, volatilization interferences tend to be troublesome in GF-AAS, and the methods for their alleviation are somewhat complex. In addition, GF-AAS normally a single-element technique, is relatively slow. Recent developments have made possible multi-element determination with GF-AAS, either with line sources or with continuum sources. However, there are some difficulties in arriving at a set of multi-element operating parameters. Continuum source multi-element AAS is further limited by deficiencies in continuum light sources, which make the limits of detection for elements with absorption lines near 200 nm, such as Se, As and Zn, poor in comparison with the corresponding detection limits with line sources.

The chief advantages of GF-AAS are excellent detection limits and relatively low in cost. However, the technique is applicable only to about 50 elements, fewer than can be determined by ICP-AES. Many elements are difficult to determine by GF-AAS because of the formation of refractory carbides. GF-AAS and ICP-AES are best viewed as complementary, rather than competitive techniques.
1.5.1.6 Comparison of ICP-AES with ICP-MS

Inductively coupled plasma mass spectrometry (ICP-MS) prefers remarkably good detection limits and the capability of determining isotopic ratios with great speed and convenience. Detection limits in the range 10^-4 - 10^-6 mg/L are obtainable with the same sample introduction systems used in ICP-AES. Significantly, most elements show similar detection limits, whereas detection limits for ICP-AES vary much more from one element to another.

Because they both use the ICP source, ICP-AES and ICP-MS show similar solute volatilization and ionization interferences, which are usually quite small. However, ICP-MS suffers from some additional problems because of the possibility of interactions in the vacuum interface and because a cool surface susceptible to condensation and deposition is introduced into the plasma. For this reason the level of dissolved solids in the analytical solutions should be kept relatively low. Precision is usually rather worse in ICP-MS than in ICP-AES, but this can be compensated for by the use of an internal standard, or by isotope dilution methods, which enable the achievement of precision and accuracy similar to that of ICP-AES. The principal disadvantage of ICP-MS is the high cost of instrumentation.

1.5.2 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy was introduced by Alan Walsh in the mid 1950s. Atomic absorption spectroscopy has proved itself to be the most powerful instrument technique for the quantitative determination of trace metals in liquids. This method provides a total metal content of the sample and is almost independent of the molecular form of the metal in the liquid. The versatility of atomic absorption spectroscopy can be realized from the fact that 60-70 elements, including most of the common rare earth metals, have been determined by this technique in concentrations that range from trace to macroquantities.

1.5.2.1 Principle

When a solution containing metallic species is introduced into a flame, the vapours of metallic species will be obtained. Some of the metal atoms may be raised to an energy level sufficiently high to emit the characteristic radiation of the metal, but a large percentage of the metal atoms will remain in the non-emitting ground
state. This ground state of a particular element is receptive of light radiation of its own specific resonance wavelength. Thus, when a light of this wavelength is allowed to pass through a flame having atoms of the metallic species, part of that light will be absorbed and the absorption will be proportional to the density of the atoms in the flame. Thus, in atomic absorption spectroscopy, one determines the amount of light absorbed. Once this value of absorption is known, the concentration of the metallic element can be known because the absorption is proportional to the density of the atoms in the flame. Mathematically, the total amount of light absorbed may be given by the expression as follows:

\[
\text{At } v \text{ the total amount of light absorbed } = \frac{\pi e^2}{mc} N f
\]

Where \(e\) is the charge on the electron of mass
\(m\) is the mass of the electron
\(c\) is the speed of light
\(N\) is the total number of atoms
\(V\) is the frequency
\(F\) is the oscillator strength
Total amount of light absorbed = constant \(N \times f\)

1.5.2.3 Instrumentation

Light of a certain wavelength, which is able to emit the spectral lines corresponding to the energy required for an electronic transition from the ground state to an excited state, is allowed to pass through the flame. Meanwhile the sample solution is aspirated into the flame. Before it enters the flame, the solution gets dispersed into a mist of very small droplets which evaporates in the flame to give the dry salt, and then the vapour of the salt. At least a part of this vapour will be dissociated into atoms of the elements to be measured. Thus, the flame possesses free unexcited atoms which are capable of absorbing radiation, from an external source when the radiation corresponds exactly to the energy required for a transition element from the ground electronic state to an upper excited level, then the unabsorbed radiation from the flame is allowed to pass through a monochromator which isolates the exciting spectral lines of light source. From the monochromator the unabsorbed radiation is led into the detector which is then registered by a
photodetector, the output of which is amplified and measured on a recorder. Absorption is measured by the difference in transmitted signal in the presence and absence of test element. A schematic diagram of the atomic absorption spectrophotometer was shown in fig. 1.6.

![Schematic diagram of the atomic absorption spectrophotometer](image)

Fig. 1.6 A schematic diagram of the atomic absorption spectrophotometer

1.5.2.4 Flames

Flame is the essential requirement in the flame spectroscopy, which is used to produce temperature in excess of 200K. This requirement can only be met by burning the fuel gas in an oxidant gas, which usually air, nitrogen oxide, or oxygen diluted with either nitrogen or argon. The flame temperatures obtained by the common fuel gases burning in (1) air (2) nitrous oxide are given in table 1.2.

The concentration of gaseous atoms, with in the flame both in the ground state and in the excited state, is influenced by 1. the flame composition and 2. the considered within the flame.
Table 1.2
Flame temperatures with various fuels

<table>
<thead>
<tr>
<th>Fuel gas</th>
<th>Temperature (K)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air</td>
<td>Nitrous oxide</td>
</tr>
<tr>
<td>Acetylene</td>
<td>2400</td>
<td>3200</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2300</td>
<td>2900</td>
</tr>
<tr>
<td>Propane</td>
<td>2200</td>
<td>3000</td>
</tr>
</tbody>
</table>

As far as flame composition is concerned, the air-acetylene mixture is suitable for the determination of about 30 metals. The propane-air flame is preferred for metals, which are easily converted into an atomic vapour state. Higher temperature of the acetylene-nitrous oxide flame is essential for the metals such as aluminium and titanium, which from refractory oxides.

1.5.2.5 The Nebulizer – Burner system

The purpose of the nebulizer – burner system is to convert the test solution to gaseous atoms and the success of flame photometric method is dependent upon the correct functioning of the nebulizer – burner system. The commonly used Beckman total consumption burner in atomic absorption spectrophotometer was shown in fig. 1.7

Fig 1.7 Beckman total consumer burner
The description of various parts of Beckman total consumer burner is as follows:

A is a solution capillary, B is the aspirating gas inlet, C is a fuel gas inlet, D is the centering screw, E is the gas inlet and F is a jacket.

1.5.2.5.1 Nebulization

The function of the nebulizer is to produce a mist or aerosol of the test solution. The solution to be nebulized is drawn up by a capillary tube by the venture action of a jet of air blowing across the top of the capillary. A gas flow at high pressure is necessary in this in order to produce a fine aerosol. The final aerosol, really a very fine fog, is mixed with the oxidizer / fuel mixture and carried into the burner. Droplets larger than about 20\(\mu\)m are trapped in the spray chamber and flow to waste, or fail to dissolve completely in the flame before reaching the observation light path.

1.5.2.5.2 Burner System

There are two types of burner used in the atomic absorption spectroscopy system. They are

a. Pre-mixed or laminar – flow burner

b. Total consumption or turbulent – flow burner

1.5.2.5.2a. Pre-mixed or laminar – flow burner

In the pre-mixed burner the aerosol is produced within a mixing chamber where the coarse and fine droplets are separated. The resulting fine droplets, virtually smog, are mixed with the fuel gas and the carrier gas (oxidant), and then mixed gases flow to the burner head. Spoilers inside the chamber ensure adequate mixing and smooth delivery to the flame. The burner head consists of an array of holes or a slot (10 cm) at which the flame burns. This type of burner serves well for flames with low burning velocities such as air-propane, air-acetylene, and nitrous oxide – acetylene and significantly longer path-length. The burning velocity of a fuel oxidant mixture is a function of the composition and usually reaches its maximum value near the stoichiometric ratio. Its advantages are 1) in the solutions made up in mixed solvents, the more volatile solvents are evaporated preferentially 2) A
potential explosion hazard exits since the burner uses relatively larger volumes of gas, but in modern versions of this type of burner hazard is minimized.

1.5.2.6 Light sources

An atom absorbs light at very discrete wavelength. In order to measure this narrow light absorption with maximum sensitivity, it is necessary to use a light source, which emits at very specific wavelengths which can be absorbed by the atom. Narrow light sources not only provide high sensitivity but also make atomic absorption a very specific analytical technique with a few spectral interferences.

There are two important external light sources are used.

A. Hallow Cathode Lamp (HCL).
B. Electrodeless Discharge Lamp (EDL).

1.5.2.6A. Hallow Cathode Lamp

The hallow cathode lamp provides a bright light source for most of the elements that can be determined by AAS. The cathode of a lamp is a hollowed-out cylinder of the metal whose spectrum is to be produced. The anode and cathode are sealed in a borosilicate or quartz glass cylinder filled with inert gas like neon or argon with low pressure. A transparent quartz window to the emitted radiation is fused to the end of the cylinder. When an electrical potential is applied between anode and cathode, some of the filled gas atoms are ionized. The positively charged ions accelerated through the electrical field to collide with the negatively charged cathode and dislodge individual metal atoms in a process called “sputtering”. The sputtered metal atoms are then excited to emission through impact with fill gas ions.

The cathode lamp is usually constructed from a highly pure metal resulting in a very pure emission spectrum of the cathode material, sometimes cathode is made from alloy of several metals. The resulting multielement lamp can be used as a source for all of the elements contained in the cathode alloy. Often the intensity of emission for an element in a multielement lamp current will increase its output intensity, but sensitivity is reduced through line broadening or self-reversal for some elements. The schematic diagram of a hallow cathode source lamp for atomic absorption of sodium was shown in fig. 1.8.
Fig. 1.8: Schematic diagram of a hollow cathode source lamp for atomic absorption of sodium

When the lamp is use, the sputtering process removes some of the metal atoms from the vicinity of the cathode and deposit elsewhere. Lamps for volatile metals such as As, Se, Hg and Cd are aged faster due to rapid vaporization of the cathode during use. Adsorption of filled gas atoms on to the inside surface of the lamp housing is another cause of lamp failure.

1.5.2.6B. Electrodeless Discharge Lamp

Electrodeless discharge lamps were originally developed as radiation sources for atomic absorption spectroscopy and atomic fluorescence spectroscopy.

The electrodeless discharge lamp consists of a quartz tube of 2-7 cm in length and 8 mm in internal diameter, containing up to 20 mg of the required element or of a volatile salt of the element, commonly the iodide for which the source is to be used is sealed inside a quartz bulb with low pressure of argon. This bulb is placed inside a ceramic cylinder on which the antenna from a radio frequency generator is coiled. When radio frequency field of sufficient power is applied, the coupled energy will vaporize and excite the atoms inside the bulb into emitting their characteristic spectrum. An accessory power supply is required to operate an electrodeless discharge lamp. Electrodeless discharge lamps are more
intense and in few cases more sensitive than comparable hallow cathode lamps. So better precision and lower detection limits can be achieved by EDL.

1.5.2.7 Monochromators

In atomic absorption measurements, the most common monochromators are prism and gratings, commercially packaged atomic absorption instrumentation commonly includes a monochromator of about ½ m focal length with a linear reciprocal dispersion in the range 16-35 \( \AA^0/\text{mm} \). The function of a monochromater is to select a given absorbing line from spectral lines emitted from the hallow cathode. For the elements where high dispersion in not necessary a resolution of the order of 0.5 \( \AA^0 \) is desirable. When the cathode in the hallow cathode lamp is made up of transition metals, the emission spectrum from the hallow cathode is so complicated that high dispersion is essential. For such cases large dispersion and high resolving mono-chromators are advantageous for resolving spectra.

1.5.2.8 Detectors

In atomic absorption spectroscopy, the photomultiplier tube is most suitable. It has good stability if used with a stable power supply. It works satisfactorily and enables to compare intense in a satisfactory manner. The schematic diagram of photomultiplier tube and power supply was shown in fig. 1.9.

![Photomultiplier tube and power supply](image)

Fig. 1.9: Photomultiplier tube and power supply
In the photomultiplier tube, there is an evacuated envelop which contains a photocathode, a series of electrodes called dynodes, and an anode. The photocathode is fixed to the terminal of the power supply as soon as a photon strikes the photocathode, an electron is dislodged and the photon is accelerated to dynode 1, resulting in the liberation of two or more electrons from this dynode. Similarly, the electrons from this dynode 1 are accelerated to dynode 2, resulting in the liberation of more electrons. Thus, the current multiplied at each dynode and the resultant electron current is received by the anode to produce an EMF across $R_L$, which goes to the external amplifier and read-out system.

1.5.2.9 Read-out Device

In most of the atomic absorption measurements, chart recorders are used as read-out devices. A chart recorder is a potentiometer using a servomotor to move the recording pen. The displacement is directly proportional to the input voltage.

1.6 SCOPE OF WORK

The present work focused on heavy metal analysis in solid waste samples which were collected during the pre and post incineration process. 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, Tl and V which are present with extensive distribution in many kinds of solid waste components. The present investigation aims to provide reference information on solid waste management and heavy metal pollution control.

1.7 CHAPTER SCHEME

The thesis has been divided into six chapters. A brief description of the contents of the chapters is given below.

Chapter 1 is an introductory part covering introduction of heavy metals, their occurrence and presence in the environment. Moreover, focus is spotlighted on entrance of heavy metal into solid waste, agriculture fields and other areas. The causes of heavy metals on environment as well its impact on human health are widely discussed. The technologies used to convert waste into energy, viz., physical technologies, chemical technologies and biological technologies are discussed. A
brief note on description of sophisticated instrumental techniques for analysis of samples, viz. AAS, ICP-AES etc. is discussed in detail.

Chapter II appraises the renewable and non-renewable sources of energy and their significance in energy development and management. Classification of solid waste, collection of solid waste and its processing are discussed. Finally, a brief note on technologies and their functioning in converting solid waste into energy in study area, technologies used for biomass conversion to energy are discussed.

Chapter III describes the general characteristics of Municipal Solid Waste. Sampling of solid waste and combustion procedures used for monitoring air emission from the stack and waste water from the neutralization pit in three seasons is briefly described. Monitoring of heavy metals is discussed with reference to pre and post combustion process. The general characteristics on heavy metals and their impact on environment and human health are discussed.

Chapter IV investigates the assessment of heavy metals present in the pre and post incinerated agricultural waste used as a raw material in the waste to energy production. General characteristics of Agriculture waste, sampling of agriculture waste, procedures used for monitoring water and air emissions in effluent treatment plant and stack monitoring respectively in three seasons are discussed. Monitoring of heavy metals is denoted with reference to pre and post combustion process.

Chapter V discusses comparison of municipal solid waste and biomass with coal combination and without coal combination in order to elicit the impact of coal in the enrichment of Gross Calorific Value and its management in generation of electricity in pre and post combustion.

Chapter VI summarizes the conclusions and major outcome of research work carried in this thesis. Based on the studies carried out in the present thesis, it describes the best way for using the municipal solid waste in the waste to energy process. Based on the studies carried out in the present thesis, the presence of the heavy metals in the municipal solid waste and agriculture waste individually and in combination of both is concluded. The recommendations on the process to be followed to make the municipal solid waste based power plants a successful. Gives details on how to act consciously in future needs to be followed.
REFERENCES


26. Cláudia, M.F. Dias and Cristina M.M. Souza (Laboratório de Ciências Ambientais, Universidade Estadual do Norte Fluminense, Av. Alberto Lamego, 2000, CEP: 28015-620, RJ, Brazil, cristal@ccb.uenf.br) & Pedro H. Monnerat (Laboratório de Fitotecnia, Universidade Estadual do Norte Fluminense, Av. Alberto Lamego, 2000, CEP: 28015-620, RJ, Brazil “distribution of heavy metals in agricultural soils from a rural area in Rio de Janeiro state, Brazil”.


