SJIF IMPACT FACTOR: 4.183 CRDEEPJournals
International Journal of Environmental Sciences Singh & Bhatnagar Vol. 3 No.4 ISSN: 2277-1948
International Journal of Environmental Sciences Vol. 3 No. 4. 2014. Pp. 220-223

Full Length Research Paper

Levels of Heavy Metals in Hazardous Waste from a Chemical Industry

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Abstract

The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. Although several adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues, and is even increasing in some parts of the world, in particular in less developed countries, though emissions have declined in most developed countries over the last 100 years. Recent data indicate that adverse health effects of cadmium exposure may occur at lower exposure levels than previously anticipated, primarily in the form of kidney damage but possibly also bone effects and fractures. The general population is primarily exposed to mercury via food, fish being a major source of methyl mercury exposure, and dental amalgam. During the last century, lead emissions to ambient air have caused considerable pollution, mainly due to lead emissions from petrol. Children are particularly susceptible to lead exposure due to high gastrointestinal uptake and the permeable blood–brain barrier.

Keywords: *Heavy Metals, Sludge sample, Digestion.*

Introduction

Heavy metals are thus commonly defined as those having a specific density of more than 5 g/cm^3. The main threats to human health from heavy metals are associated with exposure to Iron, Zinc, Copper ,Cobalt, lead, cadmium, mercury and arsenic (arsenic is a metalloid, but is usually classified as a heavy metal). Heavy metals have been used in many different areas for thousands of years. Lead has been used for at least 5000 years, early applications including building materials, pigments for glazing ceramics, and pipes for transporting water. At the end of the 20th century, however, emissions of heavy metals started to decrease in developed countries: in the UK, emissions of heavy metals fell by over 50% between 1990 and 2000 (Anonymous Report, 2001). Emissions of heavy metals to the environment occur *via* a wide range of processes and pathways, including to the air (*e.g.* during combustion, extraction and processing), to surface waters (*via* runoff and releases from storage and transport) and to the soil (and hence into groundwater's and crops). Atmospheric emissions tend to be of greatest concern in terms of human health, both because of the quantities involved and the widespread dispersion and potential for exposure that often ensues. Lead emissions are mainly related to road transport and thus most uniformly distributed over space. Cadmium emissions are primarily associated with non-ferrous metallurgy and fuel combustion, whereas the spatial distribution of anthropogenic mercury emissions reflects mainly the level of coal consumption in different regions. Exposure is often defined as a function of concentration and time: "an event that occurs when there is contact at a boundary between a human and the environment with a contaminant of a specific concentration for an interval of time (Anonymous Report, 1991) The strongest toxic properties are characteristic for inorganic metals compounds, which dissociate well and are easily soluble because they can easily penetrate through cell membranes and get into internal organs. These metals accumulate mainly in kidneys, the adrenal gland, liver, lungs, hair and skin, and they may cause high blood pressure, cancerous changes, damage to kidneys, liver and brain. In some cases they may also lead to mental disorders and loss of brain function. The general population is primarily exposed to mercury *via* food, fish being a major source of methyl mercury exposure, and dental amalgam (Sallsten et al., 1996).

Several experimental studies have shown that mercury vapor is released from amalgam fillings, and that the release rate may increase by chewing (WHO, 1991). Acute mercury exposure may give rise to lung damage. Chronic poisoning is characterized by neurological and psychological symptoms, such as tremor, changes in personality, restlessness, anxiety, sleep disturbance and depression. The Minamata catastrophe in Japan in the 1950s was caused by methyl mercury poisoning from fish contaminated by mercury discharges to the surrounding sea. A high dietary intake of mercury from consumption of fish has been hypothesized to increase the risk of coronary heart disease (Salonen et al., 1995).

The general population is exposed to lead from air and food in roughly equal proportions. In adults, inorganic lead does not penetrate the blood–brain barrier, whereas this barrier is less developed in children. The high gastrointestinal uptake and the permeable blood–brain barrier make children especially susceptible to lead exposure and subsequent brain damage. Organic lead compounds penetrate body and cell membranes. Tetra-methyl lead and tetraethyl lead penetrate the skin easily. The symptoms of acute lead poisoning are headache, irritability, abdominal pain and various symptoms related to the nervous system.

Natural as well as anthropogenic sources of cadmium, including industrial emissions and the application of fertilizer and sewage sludge to farm land, may lead to contamination of soils, and to increased cadmium uptake by crops and vegetables, grown for human consumption. The uptake process of soil cadmium by plants is enhanced at low pH (Jarup et al., 1998). Inhalation of cadmium fumes or particles can be life threatening, and although acute pulmonary effects and deaths are uncommon, sporadic cases still occur (Siedal et al., 1998, Barba et al., 1999) .Cadmium exposure may cause kidney damage. The first sign of the renal lesion is usually a tubular dysfunction, evidenced by an increased excretion of low molecular weight proteins [such as β_2-microglobulin and α_1-microglobulin (protein HC)] or enzymes [such as N-Acetyl-β-D- glucosaminidase (NAG)]. It has been suggested that the tubular damage is reversible (Hotz et al, 1994), but there is overwhelming evidence that the cadmium induced tubular damage is indeed irreversible.

Iron is a lustrous, ductile, malleable, silver-gray metal (group VIII of the periodic table). Iron is chemically active and forms two major series of chemical compounds, the bivalent iron (II), or ferrous, compounds and the trivalent iron (III), or ferric, compound. Iron can be found in meat, whole meal products, potatoes and vegetable Iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues. Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer. A more common problem for humans is iron deficiency, which leads to anemia. Water-insoluble nickel compounds including nickel sulfides, disulfides, and oxides readily enter the cell and are very potent carcinogens (Dunnick et al., 1995). The primary source of nickel in drinking-water is the leaching of metals in water network (WHO, 2005). However, food is the major source of nickel exposure in the non-smoking, non-occupationally exposed population, but nickel absorption from water, was significantly higher than absorption of nickel from beverages like tea, coffee, or orange juice and milk (Nielsen et al., 1999). Ni^{2+} induces carcinogenesis through several processes including DNA hypermethylation (H3K9 mono- and dimethylation), DNMT inhibition, DNA mutation, ROS generation, inhibiting histone H2A, H2B, H3 and H4 acetylation, converting the tumor suppressor genes to the heterochromatin, and substantial increases of the ubiquitosation of H2A and H2B (Ke et al., 2008).

Materials and Methods

The study was conducted in Chemical industry near Rajpura (Punjab) during Feburary to March 2014. The products are Caustic Soda (Flakes & Lye), Hydrochloric Acid, Stable Bleaching Power, Sodium Hypochlorite, Hydrogen and Liquid Chlorine. The manufacturing process is based on the environment friendly Membrane Cell Technology. The technology involved consists of fine control of all process parameters with world's most sophisticated Distributed Control System (DCS). Safe operation is an integral part of the DCS. The sludge sample was collected from the outlet site where the waste sludge was collected for disposal during the period (Feb to March, 2014).The standard of various metals (Lead, Cadmium, Zinc, Nickel, Copper, Iron, Calcium, Manganese,) of CRM grade were procured from M/s Merck Specialties Private ltd. The most common technique to determine heavy metals like Lead, cadmium, Nickel, Zinc, Copper, Iron, Calcium and Magnesium are atomic absorption spectrometry (AAS) and mercury can be analyzed by Mercury analyzer.

Atomic absorption spectroscopy

The majority of free atoms in the commonly used flames were in the ground stage, but that the flame didn't have the enough energy to excite these atoms (except group I elements). A light source (Hallow cathode lamp) emitting a narrow spectral line of characteristic energy is used to excite the free atoms formed in the flame. The decrease in energy is then measured.
The absorbance is proportional to the concentration of the free atoms in the flame, given by the Lambert- Beer Law.
Absorbance = $\log_{10} I_o/I_t = K.C.L$
I_o= Intensity of Incident Radiation emitted by the light source
I_t = Intensity of transmitted radiation (amount not absorbed)
C =Concentration of sample (free atoms)
K = Constant (Can be determined experimentally)
L = Path Length

Mercury analyzer

Mercury is determined by Mercury analyzer. The Mercury analyzer is a sensitive instrument designed for the precise determination of minute traces of mercury in liquid samples. Basically it is cold vapor atomic absorption spectrophotometer based on the principle that mercury vapor (atoms) absorb resonance radiation at 253.7 nm. The MA 5840 consist of low pressure mercury lamp emitting the 253.7nm line, an absorption cell, a filter, a detector with associated electrons and vapor generation system carries elemental mercury from the solution and then passes through the absorption cell.

Results

The levels of Hg, Pb, Cd, Zn, Ni, Cu, Fe, Ca, Mn in sludge sample has been presented in following table-

Table 1. Levels of various metals in various sludge sample.

S.No	Metals	Level Detectable(mg/kg)	Concentration limit recommended by CPCB(Schedule II, Rule 3(1)) in mg/kg
1	Mercury	1.06	50
2	Lead	34.6	5000
3	Cadmium	3.69	50
4	Zinc	23.55	20,000
5	Nickel	4.39	5000
6	Copper	10.04	5000
7	Iron	6415	50,000
8	Calcium	410.55	50,000
9	Magnesium	217.63	50,000

Calibration curve of Mercury is shown in figure 1-

Conc (in ng)	Abs
0	**0**
20	0.052
40	0.096
60	0.146
80	0.191
100	0.238

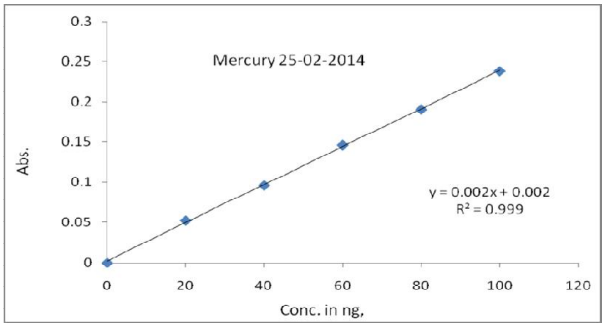

Fig 1- Calibration Curve of Mercury

Discussion

Emissions of heavy metals to the environment occur *via* a wide range of processes and pathways, including to the air (*e.g.* during combustion, extraction and processing), to surface waters (*via* runoff and releases from storage and transport) and to the soil (and hence into ground waters and crops).We can surely say that heavy metals adversely affect human system by enter into body through many ways. Mercury, lead, arsenic, cadmium, nickel, zinc, cobalt and copper etc are release in huge quantity from chemical manufacturing and other type of industries which pollute our land, air and water. Those heavy metals cause cancer, lung diseases, blindness, depression, kidney damage, urinary diseases.

The Minamata catastrophe in Japan in the 1950s was caused by methyl mercury poisoning from fish contaminated by mercury discharges to the surrounding sea. A high dietary intake of mercury from consumption of fish has been hypothesized to increase the risk of coronary heart disease (Salonen et al., 1995).

Mercury and Mercury compounds, Cadmium and Cadmium Compounds are class A metals, have concentration limit 50 mg/kg (CPCB-Schedule II, Rule 3(1)). The tested sludge sample have concentration of Mercury is 1.06 mg/kg and Cadmium is 3.69 mg/kg. Permissible Limit of cadmium is 3mg/kg.

Inhalation of cadmium fumes or particles can be life threatening, and although acute pulmonary effects and deaths are uncommon, sporadic cases still occur (Seidal et al., 1993, Barbee et al., 1999) .Cadmium exposure may cause kidney damage. Animal experiments have suggested that cadmium may be a risk factor for cardiovascular disease, but studies of humans have not been able to confirm this (Jarup et al., 1998) .However, a Japanese study showed an excess risk of cardiovascular mortality in cadmium-exposed persons with signs of tubular kidney damage compared to individuals without kidney damage (Nishijo et al., 1995). Copper, Lead and Nickel are class B metals, because their concentration limit 5,000 mg/kg. (CPCB-Schedule II, Rule 3(1)). The tested sludge sample have concentration of copper is 10.04 mg/kg; lead is 34.6 mg/kg**.** Permissible Limit of lead is 300 mg/kg. **(NEPM,** National Environment Protection (Assessment of Site Contamination) Measure 1999). The concentration of Nickel in sludge sample is 4.39mg/kg.

Calcium, Magnesium and Iron are D Class metals have concentration limit 50,000 mg/kg. (CPCB-Schedule II, Rule 3(1)).In Sludge sample concentration of calcium and Magnesium is 410.55 mg/kg and 217.63 mg/kg respectively. The concentration of iron in sludge sample is 6415 mg/kg. So to see the above effects of heavy metals .we can say that it is necessary to minimize the exposure of these heavy metals into environment by proper waste treatment and regular study of the heavy metals quantity which are released in production and take steps to minimize their exposure by appropriate methods.

Conclusion

Exposure of heavy metals like mercury, lead, cadmium, nickel, arsenic etc is the main problem for human health and environment. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. For study of these heavy metals and their concentration in the environment the sludge sample are taken out from the chemical industry which manufacture chemicals. The products are Caustic Soda (Flakes & Lye), Hydrochloric Acid, Stable Bleaching Power, Sodium Hypochlorite, Hydrogen and Liquid Chlorine. The sludge which is remained after the membrane treatment of waste material are disposed off into outlet site .From outlet site this sample are taken out and studied into a laboratory of how much concentration of heavy metals into the waste sludge? The main motive to study these heavy metals is that to know and understand how much we and our environment are affected by their exposure and what the appropriate steps we should choose to minimize their effects and to save our environment.

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