

Research Paper :

Sequential extraction and spectrophotometric estimation of heavy metals from thermal power plant generated coal fly ash and its admixtures

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ABSTRACT

An attempt is made to study the extractability of heavy metals from fly ash generated from Thermal Power Plant which is used as an admixture with cement, brick manufacturing, land filling and in agriculture. From the utilization point of view, it was notable that the total heavy metal concentrations (Cu, Pb, Zn, Ni, Fe, and Mn) in fly ash from a coal-fired power plant were lower than those limit values. A six-stage sequential extraction procedure was used to evaluate the extractability of different elements in fly ash into the following fractions: (1) the water-soluble fraction, (2) the exchangeable fraction (1M MgCl₂ at pH 7), (3) Carbonate bound (1M Na-OAC at pH 5), (4) Fe- Mn bounded (0.04M NH₂OH, HCl in 25% acetic acid), (5) Organically bound (0.02 M nitric acid and 30% H₂O₂ at pH 2 and 90°C, followed by 1.2 M ammonium acetate in 10% nitric acid) and (6) Residual metal ions (HNO₃ and HClO₄ acid digestion until dryness).

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In thermal power plant, coal is burnt at temperatures ranging around 1400-1500°C with about 20% excess air in the furnace. The utilization of flyash is 70% in Australia, 40% in UK, 40% in cement manufacturing in France (Nath, 1997). Actually flyash is extensively used in concrete as an admixture in order to reduce cost of cement. Up to 25% to 30% industrial flyash was successfully blended with ordinary Portland cement without sacrificing strength and durability characteristics (Rao *et al.*, 1999). Moreover, manufacture of Portland cement is a significant contributor of greenhouse gases (Sharma, 2006). With a view to reduction of green house gases, in this study flyash was collected from Bhusawal Thermal Power Plant, for estimation of heavy metals from fly ash admixtures utilized in cement and brick manufacturing. Coal from Bhusawal Thermal Power Plant has been also collected and made it to ash by burning at 1200-1500°C.

Utilization of solid wastes in activities such as land spreading allows industry to reuse, reduce, and recycle waste as beneficial products. Inorganic materials such as ashes from energy production (especially from coal and peat-fired power stations) and some metallurgical slugs are typical materials with potential for utilization in earthworks. However, according to Wahlstrom and Laine-Ylijoki (1996) from the Technical Research Centre of Finland, if inorganic materials and by-products, e.g., wastes, are to be utilized in earthworks, the content of harmful compounds must be low and the harmful components must be tightly bound to the matrix. Before ash residue can be utilized or deposited, according to

Steenari *et al.* (1999), its chemical as well as leaching characteristics must be known. The total element concentrations represent a source term only for the unrealistic environmental scenario in which the entire mineral structure of the solid material is dissolved. Thus, measurement of the total concentration of metals provides relatively misleading information for assessing the bioavailability and mobility of metals. In order to estimate the real bioavailability of metals and their potential toxicity, it is necessary not only to determine the total concentrations but also the different chemical forms or processes binding the heavy metals to the solid phase of the sample (Albores *et al.*, 2000). Extraction tests are widely used as tools to estimate the release potential of constituents from waste materials over a range of possible waste management activities, including recycling or reuse, for assessing the efficacy of waste treatment processes, and after disposal (Kosson *et al.*, 2002). Sequential extraction tests are designed to treat the material with different solutions, resulting in the allocation of constituents into separate fractions. Such an approach gives information on which chemical conditions are needed to obtain different extraction efficiencies. Extraction is a procedure that is widely applied to the extraction of elements from various environmental samples such as soil, sediment, airborne particulate matter, sludge, and waste (Filgueiras *et al.*, 2002). Extraction does not necessarily mean total decomposition, and the extractable recoveries of analyte are generally lower than the total concentrations. Recoveries can only reach the total values if an element is completely soluble in the extraction

solvent. Extraction studies are carried out in the assessment of worst-case environmental scenarios, in which the components of the sample become soluble and mobile (Lorenzen and Kingston, 1996). The aims of this study was to assess the total heavy metal concentrations in coal fly ash with respect to the new finnish limit values of the maximal allowable heavy metal concentrations for fertilizers used in agriculture and in forestry, as well as for materials used as earth construction agents. Furthermore, a six-stage sequential extraction process was used in order to assess the ability of different extraction agents to release heavy metals from the sample.

MATERIALS AND METHODS

The fly ash investigated in this study was obtained from the Bhusawal Thermal power plant, which uses the pulverization technique for the incineration of coal. The incineration temperature in the combustion chamber was between 1000^o and 1400^oC. The fly ash was sampled from the electrostatic precipitator of the plant. The sampling period represented normal process conditions for the plant. A coning and quartering method was applied repeatedly to reduce the wet ash sample to a size suitable for laboratory analysis. After sampling, the sample was stored in a polyethylene bottle in a refrigerator (4^oC) until the analysis was carried out.

The other samples were collected from the area of Bhusawal Thermal power plant. Five different types of sample were selected, like fine fly ash, bottom ash, dumping site ash, cement sample and brick sample. Total metal concentrations were calculated by the sum of the concentrations of the six fractions determined by the sequential extraction.

Sequential chemical extraction procedure and element determination in extract:

The sequential chemical extraction (SCE) was carried out at six fractions using multiple extractions of the fly ash (Alam *et al.*, 2006). The six fractions were identified.

- Water-soluble metal ions.
- Exchangeable (1M MgCl₂ at pH 7).
- Carbonate bound (1M Na-OAC at pH 5)
- Fe- Mn bound (0.04M NH₂OH, HCl in 25% acetic acid)
- Organically bound (0.02 M nitric acid and 30% H₂O₂ at pH 2 and 90^oC, followed by 1.2M ammonium acetate in 10% nitric acid)
- Residual metal ions (HNO₃ and HClO₄ acid digestion until dryness)

Extraction was carried out by shaking 4 g of ash

with the extractant in a polypropylene bottle. In order to minimize possible chemical and/or microbiological changes in the ash during the extraction procedure, the extraction was carried out using ash samples as sampled, instead of dried samples since, according to Kosson *et al.* (2002). It is preferable to avoid sample drying before extraction. After each extraction step, the extracts were separated from the solid residue by filtration through a 0.45- μ m membrane filter (47 mm in diameter). In order to avoid losses between the leaching stages, the filters and adhering ash particles from the previous extraction stage were also included in the next stage. After addition of 200 μ l of 65% HNO₃ in the supernatant phase (not in stage 6 because it was already strongly acidic), extracts were stored in a refrigerator (4^oC) until the element determinations. The element concentrations in the extracts (*i.e.*, stages 1–6) were determined with a S Series AA Spectrometer (Thermo Scientific), U.K.

RESULTS AND DISCUSSION

The results obtained from the present investigation are presented below :

Partitioning of heavy metals in the ash:

The distribution of heavy metals in the fly ash after a six-stage sequential extraction procedure between the water-soluble fraction (H₂O), the exchangeable fraction (1M MgCl₂ at pH 7), carbonate bound (1M Na-OAC at pH 5), Fe- Mn bound (0.04M NH₂OH, HCl in 25% acetic acid), organically bound (0.02 M nitric acid and 30% H₂O₂ at pH 2 and 90^oC, followed by 1.2M ammonium acetate in 10% nitric acid), and the residual metal ions (HNO₃ and HClO₄ acid digestion until dryness) are shown in Table 1, 2, 3, 4 and 5 and Fig. 1, 2, 3, 4, and 5. Although the total heavy metal concentrations in the fly ash were low, sequential extraction helps to evaluate the extractability of different heavy metals. According to Wahlstrom and Laine-Ylijoki (1996) from the Technical Research Centre of Finland, knowledge of the extractability is important if waste is to be utilized. Because the total concentration of Cd was very low, there was no partitioning for these heavy metals shown. When the sequential extraction procedure is applied for the partitioning of heavy metals in environmental samples (e.g., ash, sludge, sediment, or soil), the ability of different extracting agents to release metal ions depends on their association with specific fractions in the sample. Extractant such as electrolytes, weak acids, and chelating agents release metals from coordination sites, while strong acids and redox agents are capable of releasing additional quantities of metals as a result of the decomposition of the solid matrix (Albores

et al., 2000, Kosson *et al.*, 2002, Filgueiras *et al.*, 2002 and Lorenzen and Kingston, 1996).

The residual fraction, in which the mineral acid mixture of HNO₃ and HClO₄ is used, was the predominant matrix for Cu (78.7%), Pb (93.3%), Zn (85.1%), and Ni (83.7%). This kind of strong mineral acid mixture is never found in nature. The residual fraction is non-mobile and is potentially the least harmful. The metals associated with this fraction are retained within the crystal lattice of minerals and inside crystallized oxides and can only be mobilized as a result of weathering, and therefore have only very long-term effects. Thus, this fraction is an assessment of the "worst case environmental scenario" in which the metals of the coal fly ash become soluble and mobile (Filgueiras *et al.*, 2002). The organically bound, for which a combination of H₂O₂/NH₄OAC is used, corresponds to metals that are organically bound or occur as oxidizable minerals, e.g. sulphides (Filgueiras *et al.*, 2002). Because metals bound to this fraction can be released under oxidizing conditions, an oxidation process is usually applied to leach out metals associated with the above-mentioned phases (Filgueiras *et al.*, 2002). Hydrogen peroxide (H₂O₂), which is used as an oxidizing reagent in this fraction, is a strong oxidant (E° = 1.77 V). In general, hydrogen peroxide applied to a heated medium (e.g. at 85°C) is the reagent preferred for dissolving organic matter as a compromise between the complete degradation of organic matter and the minimum alteration of silicates, heating promotes the oxidation process. Besides the extraction of cations by ammonium ions, partial removal of some elements may occur due to complexation with acetate anions (Arunachalam *et al.*, 1996).

The use of hydroxylamine hydrochloride (NH₂OH-HCl), which is a strong reducing agent, as extractant for the easily reduced Fe-Mn bound fraction simulates anoxic conditions that are likely to occur in natural media (Yusfi and Bermond, 1997). The Fe and Mn oxides act as cement or are present as nodules between the particles or coating them. The elements are strongly bound to these oxides but are thermodynamically unstable in anoxic conditions. The metals in this fraction can be mobilized by increasing the reducing or oxidizing conditions in the environment (Kazi *et al.*, 2005). The exchangeable fraction, *i.e.*, extractable with 1M MgCl₂ at pH 7, gives an indication of the amount of metals bound on the surface of the particles, as well as of metals that are released as acid-soluble salts such as carbonates. This fraction is bio-available and corresponds to the form of metals that are most available for plant uptake; metals can be released by merely changing the ionic strength of the medium. The

metals extracted in the water-soluble fraction are relatively mobile and thus may be readily extractable and are potentially bio-available. In water extraction, the driving forces influencing the partial dissolution of matrix components are solubility, the diffusion rate of the element forming part of the matrix, and the wash off of compounds on the surface of the matrix. This fraction is the most readily available metal fraction from the point of view of the environment, and thus the extraction of metals in this fraction is a major environmental concern (Filgueiras *et al.*, 2002). Water-soluble species yield very important information required in evaluating the risk of environmental pollution by dumping waste, since, in nature, water is an important vector of harmful compounds into the environment (Kosson *et al.*, 2002). It is worth noting that the water used in this fraction was distilled and acidified with HNO₃, and thus had a higher ionic strength than demineralized water. This type of water in fact is similar to the acidic rainwater which percolates through the waste material in normal conditions in a landfill, (Hage *et al.*, 2004 and Svensson *et al.*, 2005).

Data of Table 1, 2, 3, 4 and 5 show the partitioning of heavy metals in fly ash and its admixture, in which only Fe shows the maximum extraction ability with reducible (Fe-Mn bound) fraction and oxidizable (organically bound) fraction. This type of oxidizing and reducing agents can be occurring in nature hence the leaching of Fe in ground water may be possible. For the other metals (Zn, Ni, Cu, Pb and Mn) the maximum extractable amount is observed in the residual fraction other fractions are comparatively very low. Although metals are extractable in all fractions, the highest concentrations of these metals occurred in the residual

Table 1 : Concentration of heavy metals in fly ash

Fraction	Zn	Ni	Cu	Fe	Pb	Mn
Water soluble	0.13	0.09	0.10	0.19	0.37	0.03
Exchangeable	0.78	0.87	0.79	1.23	0.78	2.11
Carbonate bound	3.57	3.97	1.71	0.49	4.17	4.01
Fe-Mn bound	2.50	3.20	0.45	31.12	3.39	10.17
Organically bound	8.71	3.19	0.77	29.15	5.60	22.13
Residual	54.5	31.29	21.9	18.56	10.28	41.23

Table 2 : Concentration of heavy metals in bottem ash

Fraction	Zn	Ni	Cu	Fe	Pb	Mn
Water soluble	0.22	0.17	0.21	0.40	0.22	0.09
Exchangeable	0.83	1.16	0.51	2.46	0.75	1.21
Carbonate bound	3.87	3.19	0.93	0.98	3.94	3.23
Fe-Mn bound	1.23	4.35	0.27	36.23	3.78	9.55
Organically bound	4.74	4.12	0.83	34.05	7.98	19.37
Residual	13.25	27.9	15.84	19.75	18.44	38.89

Table 3 : Concentration of heavy metals in cement

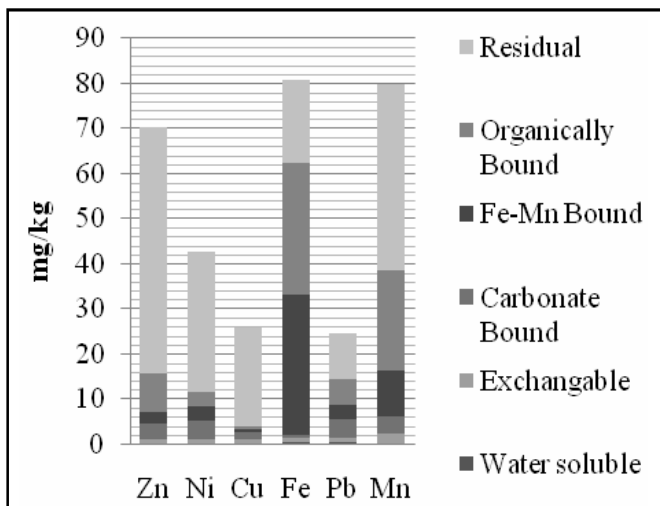
Fraction	Zn	Ni	Cu	Fe	Pb	Mn
Water soluble	0.19	0.12	0.18	0.23	0.35	0.11
Exchangable	0.64	0.81	0.92	1.69	0.67	2.62
Carbonate bound	3.11	3.56	1.45	0.74	4.55	3.19
Fe-Mn bound	2.17	3.26	0.71	32.16	4.99	11.71
Organically bound	8.01	3.85	1.27	31.65	6.52	21.33
Residual	51.57	29.78	23.12	21.77	19.78	44.49

Table 4 : Concentration of heavy metals in bricks

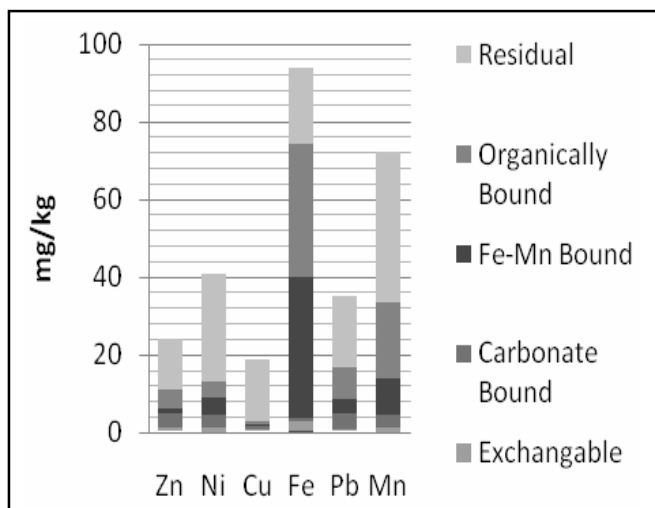
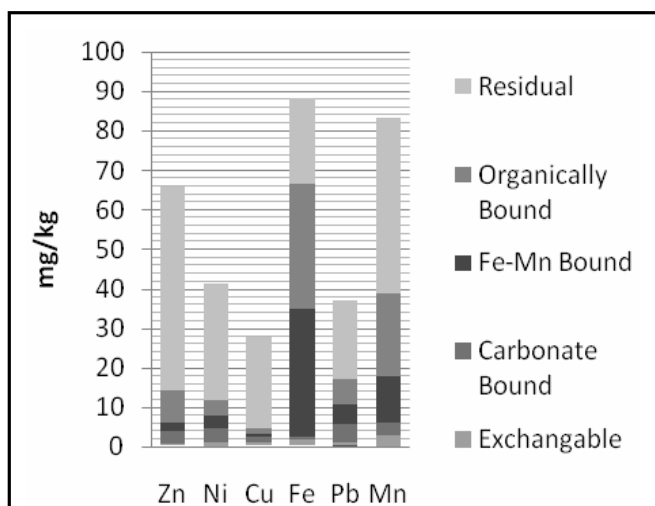
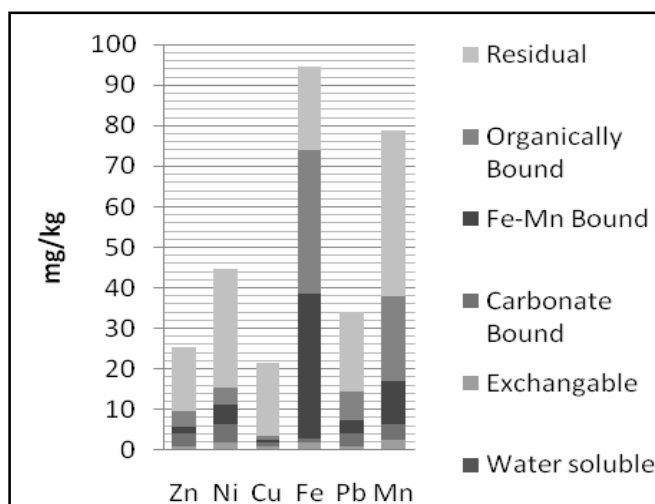
Fraction	Zn	Ni	Cu	Fe	Pb	Mn
Water soluble	0.29	0.35	0.19	0.12	0.23	0.21
Exchangable	0.73	1.71	0.64	1.69	0.69	2.23
Carbonate bound	3.17	4.37	1.13	1.08	3.27	4.12
Fe-Mn bound	1.65	4.86	0.73	35.57	3.12	10.58
Organically bound	3.73	4.15	0.88	35.35	7.11	20.75
Residual	15.71	29.12	17.83	20.57	19.53	40.91

Table 5 : Concentration of heavy metals in dumping (land fil) site

Fraction	Zn	Ni	Cu	Fe	Pb	Mn
Water soluble	0.22	0.13	0.12	0.13	0.14	0.19
Exchangable	0.83	0.83	0.41	1.81	0.50	1.03
Carbonate bound	3.87	3.78	0.86	0.78	3.18	3.36
Fe-Mn bound	1.23	3.85	0.38	35.97	3.03	7.86
Organically bound	4.74	3.27	0.69	33.12	6.02	17.22
Residual	12.85	25.19	16.66	18.15	16.44	37.12

**Fig. 1 : Partitioning of heavy metals in fly ash**

fraction (HNO_3 and HClO_4). This kind of strong mineral acid mixture is never found in nature, and therefore the metals of the coal fly ash and its admixture that are distributed in the residual fraction are not likely to be dissolved easily under the conditions normally found in

**Fig. 2 : Partitioning of heavy metals in bottom ash****Fig. 3 : Partitioning of heavy metals in cement****Fig. 4 : Partitioning of heavy metals in bricks**

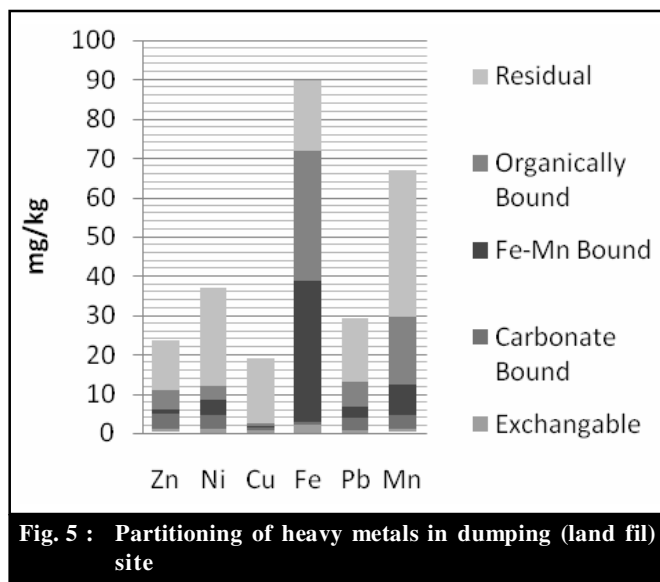


Fig. 5 : Partitioning of heavy metals in dumping (land fill) site

nature. Therefore contamination of ground water by these metals can occur but in much lower amount which could not harm the human life.

Conclusion:

From the study following conclusions can be made:

Fly ash is actually a solid waste. So, it is priceless. If it can be used for any purpose then it will be very good for both environment and economy. Use of this fly ash as a raw material in cement and bricks manufacturing is an effective means for its management. It can obviously reduce the production cost of cement and bricks manufacture. It can be concluded that power plant waste is extensively used in concrete as a partial replacement for cement and an admixture and used as a suitable for conventional materials in road construction, bricks manufacturing and agriculture. Although metals were extractable in all fractions, the highest concentrations of most of the metals occurred in the residual fraction (HNO_3 and HClO_4). This kind of strong mineral acid mixture is never found in nature, and therefore the metals of the coal fly ash that are distributed in the residual fraction are not likely to be dissolved easily under the conditions normally found in nature.

It can be concluded that the heavy metals in coal fly ash could be extracted quantitatively by the sequential extraction procedure used in this work. Therefore, contamination of ground water by these metals can occur but in much lower amount which could not harm the human life. This means that if the coal fly ash is utilized, e.g., as an earth construction agent or in agriculture the proportion of metals partitioned in the residual fraction is not easily leached out. From the study on the fly ash, it is observed

that geotechnical properties of fly ash are suitable for used in cement and bricks manufacturing and in the agricultural use.

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