

## Relevance of Various Leaching Factors on Mobility of Heavy Metals from Indian Coal Fly Ash

Renu Tiwari<sup>1</sup> Manoj Kumar Tiwari<sup>2</sup>

<sup>1</sup>PhD Scholar, Civil Engineering, Dr. C. V. Raman University, Bilaspur, Chhattisgarh

<sup>2</sup>Professor, Dr. C. V. Raman University, Bilaspur, Chhattisgarh

**Abstract:** Despite the variety of utilization efforts, huge amounts of fly ash are being ultimately dumped in the ash dykes. Many heavy metals present in fly ash like As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn, etc. may get mobilized in the leachate under favourable conditions and pollute soil, water sources and, thus finally possess a health or environmental risks. Hence, from the environmental point of view, it is a matter of a great concern. This study explores the relevance of various leaching factors like, the pH, time duration, particle size, leachant, Liquid to Solid (L/S) ratio, and leaching test employed with respect to the mobility of some heavy metals from the Indian fly ash.

**Key words:** Fly ash, Heavy metals, leaching, pH, pollution, Liquid- Solid Ratio, Coal

### Introduction

Coal-based power generation has the negative aspect as large amounts of coal fly ash. The characteristics of coal fly ash mainly depended on the firing environment and the quality of coal (Sanjuán and Argiz, 2022). As the largest energy consumer (3.4%) of the global energy consumption, India holds 6<sup>th</sup> rank in the world (Pandey et al., 2011) with 3<sup>rd</sup> rank as coal based power generation (Yousuf et al., 2020). The majority of power demand in India, is met up by coal-based power plants, contributing about 60–65% percent of total installed power capacity of the country (Kumar and Nandi, 2021) and coal consumption is about 759.02 Million Tonnes for the year 2021-22 (CEA, 2022) resulted in a huge amount of ash as the by-product. Ash content (30–60%) in the Indian coal is quite high (CEA 2022, Aich et al., 2020; Basu et al., 2009; Bhatnagar and Chouhan, 2012; Pandey, 2014). Present rate (73.13 million tonnes/yr) of coal utilization (about 70% as the fuel) the per year fly ash generation rate presently in India is nearly 131.09 million tonnes (Singh and Gupta, 2014; Tiwari et al., 2016). Fly ash utilization rate in India (more than 38%) as compared to urbanized countries (more than 70%) is still far behind (Pandey et al., 2011). According to a report of the Central Electricity Authority (CEA) New Delhi, March, 2016—for one megawatt thermal power generation approximately requires 2000 tonnes of raw coal resulting in about 800 tonnes (i.e. 40% of coal used) of fly ash with an average ash content of 33.23% (664.6 tonnes) whereas at present, installed thermal capacity is 207220.50 MW for the year 2020-21 (first half) results a huge amount of fly ash (106 MT) (CEA, 2021), a key environmental concern due to its size and contains toxic metals (Amran et al., 2022) and other harmful substances in an adequate concentration to be capable of leaching out over a period of aging which is leading to release and spread of pollutants to soil, surface and groundwater sources (Altıkulaç et al., 2022; Amran et al., 2022; Pandey et al., 2011). Fly ash utilization rate of the first half of the year 2020-21 is about 79.18 %, which is far behind the predetermined target of the government as 100% (CEA, 2021). The possible usages of coal fly ash are summarized in figure 1.

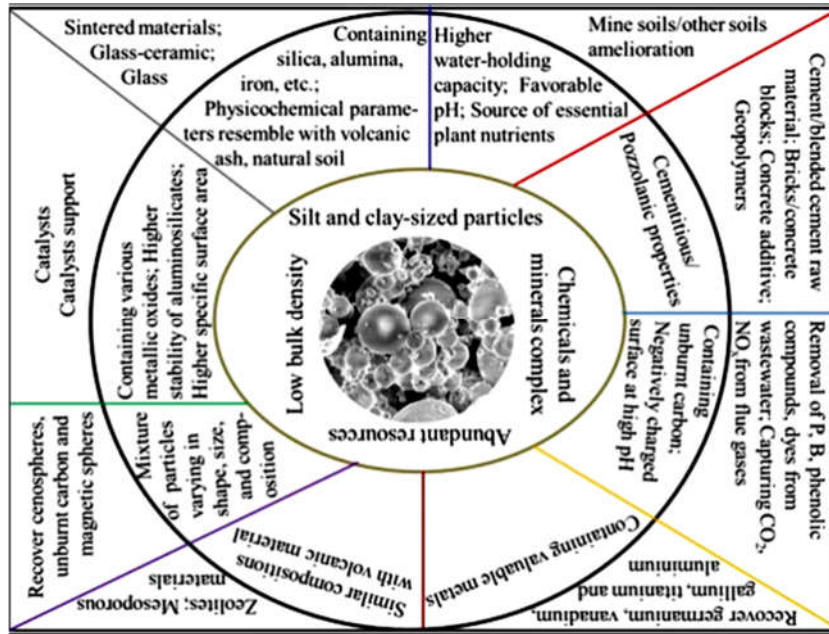


Figure 1: Utilization areas of coal fly ash (Yao et al. 2015)

**Table 1: A Summary of Fly ash Generation and its Utilization**

Description	2017-18	2018-19	2019-20	2020-21	2021 - 22
Nos. of Thermal Power Stations	167	195	197	202	200
Coal Consumed (million tons)	437.41	482.97	523.52	549.72	759.02
Average Ash Content (%)	33.24	33.87	33.02	33.50	35.68
Flyash Generation (million tons)	196.44	217.04	226.95	232.56	270.82
Flyash Utilisation (million tons)	131.87	168.40	189.01	214.91	259.86
<b>Percentage Utilization</b>	67.13	77.59	83.28	92.41	<b>95.95</b>

Source: [https://cea.nic.in/wpcontent/uploads/tcd/2022/08/Fly\\_ash\\_Generation\\_and\\_utilisation\\_Report\\_2021\\_22-1.pdf](https://cea.nic.in/wpcontent/uploads/tcd/2022/08/Fly_ash_Generation_and_utilisation_Report_2021_22-1.pdf) - accessed on 28 February 2023

If hundred percent coal fly ash is not utilized or disposed off appropriately, it might be harmful to our living milieu due to the release of heavy metal compounds from huge accumulation and also deteriorate the character of the vicinity (Amran et al., 2022; Verma et al., 2021; Pandit et al., 2011).

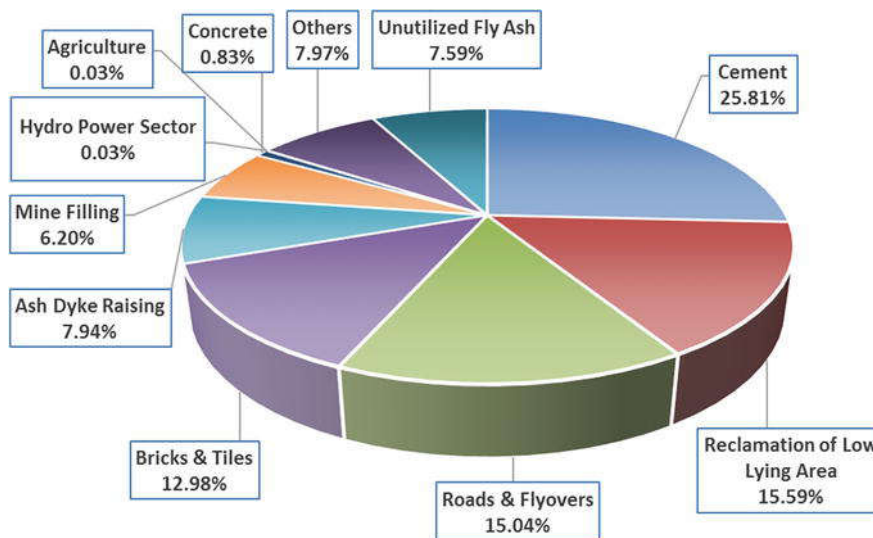


Figure 2: Fly ash utilization in India during the year 2020–2021 as per CEA report, Aug-2021, Ministry of Power, INDIA

In context of the huge amount of generation of fly ash and its less utilization trends and final disposal may consequently release heavy metals by leaching, poses a severe pollution of land, water sources, and aquatic life (Amran et al., 2022; Pandey, 2014; Pandit et al., 2011). Management of fly ash is commonly done in the wet slurry form, which is alkaline in nature (pH of 9.7 and TDS of 7290 mg/l) to the ash pond (Singh et al., 2010) which may be accountable for water and land pollution in the vicinity, by percolation of leachate (Verma et al., 2021, Gupta and Paul, 2016). The degree of impact on the environment of waste containing toxic substances, i.e. heavy metals is not only dependent on the type of pollutants and their concentrations, but mainly on their mobility from the waste (Velayatzadeh, 2023; Kalembkiewicz and Sitarz-Palczak, 2015).

### Chemical characteristics of Indian fly ash

The chemical characteristics of fly ash are greatly associated with properties of coal used, burning atmosphere, along with practices used for handling and storage and thus main components of bituminous coal fly ash as silica, alumina, iron oxide, and calcium, with some amount of unburned carbon (measured by the loss on ignition) (Nayak et al., 2022; Roulia, M., et al., 2022; Ram and Mohanty, 2022; Ahmaruzzaman, 2010; Lokeshappa and Dikshit, 2011; Prasad and Mondal, 2008). The main mechanisms to transport the metals from coal to fly ash are the volatilization, melting, decomposition, the formation of new materials and oxidation (Pandey, 2014). The coal fly ash is a combination of ferro – alumino – silicate and containing substantial amounts of Ca, K, and Na (Chaudhary et al., 2009; Jastrow et al., 1981) with a number of possible toxic heavy metals like Pb, Zn, Cd, Ni, As, and Co, which would be able to pollute soil, water sources, if present in higher concentrations (Bhattacharjee et al., 2013). Fly ash contains major elements like SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe with a significant amount of Ca, Mn, Potassium, Phosphorous and Sulphur (Kumar, 2005; Aswar, 2001; Mohapatra, and Kanungo, 1997; Ivanova, 2011; Lokeshappa and Dikshit, 2011; Singh, 2013; Ibrahim, 2015). It was confirmed that the Indian coal ash has major content of SiO<sub>2</sub>, a considerable amount of oxides of Ca, Mg, K, P, S, and micronutrients (Cu, Fe, Mn, Zn, etc.), a low content of N (especially in pond ash), and absence of humus (Kumar, 2005; Ram et al., 2011).

**Table 2: Chemical compositions of some Indian Fly Ash**

Reference	Source	Composition (%)					
		LOI*	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
Kumar et al., 2021	Thar Power Plant	NA	35.2	16.82	17.9	16.41	<0
Siddique (2003)	Thermal Power Plant, Bathinda	1.9	55.3	5.3	25.70	5.6	2.1
Kumar and Kumar (2010)	Thermal Power Plant, Chhattisgarh	1.59	60.48	4.52	28.15	1.71	0.47
Chacko et al. (2013)	BSP, Chhattisgarh	8.0	58.0	2.0	22.0	1.0	0.8
Tiwari and Ghiya (2013)	Kota Super Thermal Power Station	0.7	58	4.6	29	1.9	0.8
	Suratgarh Super Thermal Power Station	0.9	57	5.5	30	1.1	0.54
Mahure et al. (2014)	Thermal Power Station, PARAS, Akola	-	58.55	3.44	28.20	2.23	0.32
Ghosh and Goel (2014)	Kolaghat Thermal Power Plant	-	54.77	0	37.27	0	-
Vimlesh and Giri (2010)	Parichha thermal power station	-	61.5	3.6	31.2	1.0	1.40

\*LOI – Loss on ignition

Alterary (2021), Bhatt et al. (2019) and Praharaj et al. (2002) reported that according to physical and chemical properties, Indian fly ash characterization has a wide range of variation. It was also reported that the chemical composition of Indian fly ash broadly indicates the presence of SiO<sub>2</sub> (40 – 65 %), Al<sub>2</sub>O<sub>3</sub> (15–30 %), Fe<sub>2</sub>O<sub>3</sub> (5 – 10 %), a small percent of CaO (0 to 8%), MgO (0 to 6 %), alkalies and un-burnt carbon (Pandian, 2004;

<http://www.cpcb.nic.in/newitems/24.pdf> - accessed on 30 July 2016). The Indian fly ash contains higher amount of SiO<sub>2</sub>, Cao and alkaline oxides and show a higher pH, when compared to the pond and bottom ash (Alterary, 2021; Pradhan and Deshmukh, 2008; Pandian, 2004). The pH of fly ash ranges from 4 to 12 and mostly makes it alkaline in nature due to the presence of less amount of sulfur in coal, hydroxides and carbonates of Ca and Mg (Bhatt et al., 2019; Tripathi et al., 2004; Kumar, 2005; Ram and Masto, 2010; Jabeen et al., 2010).

### **Heavy metals in fly ash**

Heavy Metals are defined as elements in periodic table having the atomic number greater than 20 or densities more than 5g/cm<sup>3</sup>, usually exclusive of alkali metals and alkaline earth metals (Cygan-Szczegieliak and Stasiak, 2022; Sherene, 2010; Tchounwou et al., 2012; Dwivedi and Rajput, 2013). The major environmental problems with heavy metals are that they are being subjected to bioaccumulation and have toxic property, thus possibly will pose a threat to life when exceeding a certain level of concentration (Altıkulaç et al., 2022; Jaishankar, 2014; Sherene, 2010).

The amount of toxic constituents presents in coal fly ash is mainly depends on the quality of coal used (<http://www.thehindu.com> – accessed on 16 August 2016). Traces of toxic constituents are present in fly ash as non-degradable pollutants like arsenic, boron, beryllium, chromium, cadmium, mercury, lead, manganese, selenium, strontium, thallium and vanadium, along with dioxins and polycyclic aromatic hydrocarbon compounds (Altıkulaç et al., 2022; Pandey, 2014; Lokeshappa and Dikshit, 2011; Senapati, 2011; Pandey, 2014; Singh et al., 2014) and may lead to release of potentially toxic substances into soil, surface water and groundwater, whereas the heavy metals – arsenic, mercury, cadmium and lead, that causes a great apprehension (Altıkulaç et al., 2022). Heavy metals Co, Cr, Cu, and Ni remain associated with the iron oxide's fraction and these elements having relatively low mobility (Cr, Cu, Pb and V) show affinity to silicates and glass fraction (Nugteren et al., 2002; Jabeen et al., 2010). Amongst a variety of elements particularly As, Ba, Br, Co, Cr, Ga, Hg, Ln, Mn, Nd, Ni, Pb, Sb, Sn, Zn, Se, S and V in coal are volatile to a significant extent in the combustion process (Kelechi and Adamu, 2022; Saha and Sinha, 2015; Singh, 2013) and on the other hand, the elements Ce, Cs, K, Mg, Mo, Na, Nb, and Rb show to have smaller fractions volatilized during combustion, whereas Si, Fe, Ca, Sr, La, Sm, Eu, Tb, Py, Yb, Y, Se, Zr, Ta, Na, Ag, and Zn are either not volatilized or show merely minor tendency related to the geochemistry of mineral substances (Altıkulaç et al., 2022; Singh, 2013; Iyer 2002). These elements can become bio-available to the plants and animals in their process of geo-cycling under varying natural environmental conditions such as Eh, pH and water action. The majority of these elements is relatively stable due to its present in the core of the fly ash and is probably because they are not volatilized in the combustion process (EI-Mogazi et al., 1988). The possible threat covers a wide spectrum of our environment including land use problems, plants, animals and humans (Baba, 2000a, b, and c).

### **Leaching tests**

Leaching tests (as long term and short term leaching) are effective tools to estimate the potential release of heavy metals from wastes (fly ash) to assess and predict environmental impact over a wide range of possible waste management actions — during recycling or reuse, for assessing the effectiveness of waste management processes, and after disposal (Mizerna and Król, 2023; Singh et al. 2010; Pandey, 2014; Tiwari et al., 2015; Bhatnagar, 2012; Singh et al., 2014)

Usually, batch/shake and column leaching methods are considered as laboratory leaching experiments and are employed for fly ash leaching and batch leaching method,

considered as most economical and rapid method which can help us to quickly obtain the kinetic parameters of leaching tests to observe the leaching characteristics of trace metals (Singh et al. 2011). Shake test was reported (Singh, 2013) as a poor indicator of conditions and thus can only be useful to a limited extent.

Column leaching test is more close to the conditions (Mizerna and Król, 2023), the flow of the leachant in is gravity influence and the solid to liquid ratio is more closer to the real field condition, particle size distribution and pore structure, and solute transport found in the field, whereas, shake tests provide information of total quantity of an element leachable (Singh, 2013; Ram et al., 2007). In a leaching study of fly ash, it was reported by Sarode et al (2010) that the heavy metals concentration in toxicity characteristic leaching procedure (TCLP) was higher than the concentration of metals found in the batch leach test. During the study, it was observed that the Cd was not leached at all from any sample in batch leach as well as TCLP tests, whereas Ni and Cd did not leach from the fly ash samples when the batch leach test was used (Sarode et al 2010). Bhatnagar and Chouhan (2012) used open column percolation experiments as a long-term leaching study for selected heavy metals as the physical set up of the open columns which are more closely resembles the field conditions. In one more leaching study (Ram et al., 2007) by column and shake test of Indian fly ash sample, the observed metals concentration order followed: buffer column > aqueous column > aqueous shake > buffer shake test. The metals (As, Se, Cr, Pb, V, Zn, etc.) mobility in TCLP was higher than that of batch leaching tests results for the sample of a fly ash (Sandeep et al., 2016).

**Table 3: Literature concerning leachability of metals from Indian fly ash**

References	Sources	Protocol	Leachant	pH	L/S Ratio	Time	Findings
Das et al., 2021	NTPC, PVT LTD.) Talcher, Odisha	Acid digestion	6 M HCl	NA	1:3	2 hr	Cr, Ni, and Cu are in greater concentration (70 to 87 mg/L) over other metals and As and Pb are found to be least
Kapoor and Christian (2016)	Super Thermal Power Plant in India	Column Test method (Meteoric Water Mobility Procedure (MWMP))	Meteoric water	varied	NA	NA	Cr and Ni did not leached, As, Mn and higher Zn in acidic pH, Cu was low due to precipitation, Cd solubilized in acidic pH.
Sarode et al. (2010)	Bhusawal Thermal Power Plant	batch leach test and TCLP	Deionised water and 1M sodium acetate buffer	4.99	5:1	24 and 18 hr	Cd was not leached at all. In batch test Ni and Cd has no mobility but Mg and Cu show higher and Fe has a lower solubility with DI water. The metals in TCLP have higher concentrations than batch test.
Shivpuri et al. (2012)	thermal power plants in Maharashtra	SEP and TCLP	acetic acid	2.88		10 minutes	In TCLP, Ca leached more and in SEP test As, Cr, Mn, Zn, Cd, Ba, Pb and Co have maximum leaching in acid soluble (AS) phase.
Prasad and Mondal, 2008	Chandrapura and Ramagundam Thermal power plant	Cascade Method	Distilled water	4.0	20 to 100	18 hr	At L/S 20, Fe showed maximum leachability while Cd showed minimum leachability. The heavy metals were found in order of Fe>Zn>Mn>Cu>Cr>Pb>Ni>Cd
Singh et al. (2010)	Indian fly ash	Serial batch leaching test	NA	NA		NA	Mn, Zn, Ca, As and Mg show higher concentration in the leachate at low L/S (Liquid solid ratio) of 4 and 8.
Pani et al. (2016)	JSPL, Raigarh and OPGC, Sambalpur	Batch leaching	Deionised water	NA		7 days	concentration of Pb, Zn, Cu and Ni is higher as compared to Cd, As, Co and Hg in both the fly ash samples
Nayak, 2015	Talcher thermal power station (TTPS), Odisha	Acid digestion	Mineral acids - (HCl, HNO <sub>3</sub> , oH <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> )	NA		4h	Rate of extraction of Al is higher with HCl and HNO <sub>3</sub> and both gives satisfactory result for Fe. oH <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> is suitable leaching agents
Singh et al. (2011)	Indraprastha Power Station, Delhi.	batch Test	Extraction fluid Aqueous Solution Buffer solution	4.93, 7 10 to 11		168, 336, 504 and 672 hours	The leachability in fly ash is affected by time of leaching.
Mohapatra, and Kanungo, 1997	NALCO	Batch Test	Distilled water	3 to 10		24 hr to 30days	The initial leaching rate of Ni, Co and Pb were more rapid than of Hg and Cr
Sivapullaiah and Baig (2010)	Tamil Nadu and Andhra Pradesh	Van der Sloot et al. (1984) method	NA	2 to 10		18 hr	L/S ratio is a major factor for leachability and mobility of the heavy metals is highly affected by the pH.
Ram et al. (2007)	TPP of Neyveli Lignite Corporation (NLC),	Shake and column	Water and sodium acetate buffer.	7 and 4.9	10:1	1 day to 4 weeks	The leaching can be controlled by its concentrations in the LFA, association with the ash particles, the pH and the leaching duration.
Singh, 2013	NA	Shake and Column	Deionised water and buffered acidic medium	NA	NA	24hr and 18 hr	Only Ca and Mn were leached for the entire period whereas, Fe, Pb, Cu, Zn, Mn, Na and K were intermittent.

### The leaching factors

From coal combustion residues (CCBs) the leachability of heavy metal is identified through a slow procedure and even with long leaching duration the solid–liquid phase equilibrium may not be achieved (Ibrahim, 2015). Mobility of heavy metals is controlled by the factors dissolution of primary solids and precipitation/sorption reactions (Pandey, 2014). There may be a number of factors that could affect the leachability of heavy metals in fly ash like mode of occurrence in the feed coal, the combustion conditions, and role of sorption/desorption, redox conditions and, most importantly, the pH (Mizerna and Król, 2023; Ibrahim, 2015; Izquierdoa and Querol, 2012; Brunori et al., 2001), properties and composition of fly ash (Ibrahim, 2015; Singh, 2013; Zandi and Russel, 2007) with other factors like leachant

composition, solubility of chemical compound, and surface area of the solid and the size of sample and grain size distribution, leachant volume, pH, and leaching duration of the test are considered as critical variables of leaching (Kim, 2005). It was also reported that the mobilization of heavy metals from fly ash was greatly influenced by various environmental factors such as leaching, percolation, pH, the age of fly ash, ion exchange, precipitation, sorption, deposition and transformation (Mizerna and Król, 2023; Sinha, 2005; Pandey, 2014). Test conditions of leaching like liquid to solid (L/S) ratio, leachant pH, particle size, temperature and leaching time also have an influence on leachability of fly ash (Mizerna and Król, 2023; Kalembkiewicz and Sitarz-Palczak, 2015; Kulkarni, 2015; Nayak, 2015; Singh et al., 2010).

## The pH

The pH is most important and influencing parameter for leaching, thus initial pH of the waste sample should also be considered during final leaching experimentation (Tiwari et al., 2015; Roy and Berger, 2011). The pH of fly ash ranges from 4.5 to 12.0 (Bhatt et al., 2019; Basu et al., 2009), but the majority of the worldwide fly ashes, including India, is alkaline in nature (Ram et al., 2011; Singh et al., 2014a). The source of fly ash, types of coal used, and an amount of Ca and S concentration, influences the pH of fly-ash and accordingly it can be acidic or alkaline (Bhatt et al., 2019; Basu et al., 2009; Izquierdoa and Querolb, 2012; Singh et al., 2014a). Based on Ca/S balance and the pH, fly ash can be classified into three main groups — strongly alkaline ashes (pH 11 to 13) (van der Sloot, 1997), mildly alkaline ashes (pH 8 to 9) (Querol et al., 2001) and acidic fly ash. The acid-base behaviour of the fly ash is important, if the pH is alkaline ( $> 10$ ) after 10 minutes, the fly ash is said to be alkaline and if the pH is neutral or acidic ( $< 7$ ) after 10 minutes, the fly ash is said to be acidic in nature (Prasad and Mondal, 2008).

Initially, when fly ash comes in contact with water, the alkaline elements present on its surface will tend to dissolve rapidly and move into solution (Kapoor and Christian, 2016; Singh et al., 2011) but, through successive increase in pH and element concentration, re-precipitation of elements may possibly form more stable secondary solids (Ruhl et al., 2010). The elements present in coal fly ash reveal varying behaviour for different leaching conditions like its pH (Shivpuri et al., 2011) and mobility of the elements present in fly ash is principally pH dependent (Singh et al., 2014a; Sivapullaiah and Baig, 2010; Ram et al., 2007). The maximum amount of heavy metals may gets released under acidic environment i.e. decreasing pH (Tiwari et al., 2015; Pani et al., 2016; Vitkova et al., 2010; Singh et al., 2010; Sivapullaiah and Baig, 2010; Chaudhary and Banerjee, 2007) whereas, generally metal solubility decreases with increasing pH (Sivapullaiah and Baig, 2010; Sarode, et al., 2010).

The pH of the ash-water system is not static, but changes over time, hence mobility of most of the elements from fly ash is clearly pH sensitive (Mizerna and Król, 2023) thus, alkalinity of fly ash intensify the mobility of a large number of trace elements of anxiety such as Cd, Co, Cu, Hg, Ni, Pb, Sn or Zn among others, but at the same time, it enhances the release of oxyanions such as As, B, Cr, Mo, Sb, Se, V and W (Izquierdoa and Querolb, 2012). The trace element mobility in water is heavily pH-dependent (de Groot, 1989). The leachability of Cd, Cu, Fe, Ni, and Pb was reported as pH dependent (Singh et al., 2014a). The actual amount of toxic elements released from fly ash in natural water (pH 7 to 8.5) from stockpiles of fly ash depends largely on the pH, bonding between the element and fly ash, its chemical form and the physiochemical properties of water (Fulekar and Dav, 1991). It was also reported that the leachability in the alkaline pH of Fe and Cd in Indian fly ash samples was found maximum, whereas, in acidic solution, the concentration of Cu, Cr, Ni and Pb were found maximum (Singh et al., 2014a).

Limited removal of Pb and Fe from fly ash during a leaching study, may govern by resulting high pH in the leachates, which was even less than the other metals Cu and Mn and the leachability of trace elements will depend more or less on the leachability of iron (Sarode et al., 2010) as Fe is tightly bound to the ash and does not leach easily (Shivpuri et al., 2011). The rate of extraction of Al and Fe increased sharply with increasing acid concentration (Nayak, 2015).

It was also reported that the varying pH may established in different seasons (pre-monsoon, monsoon, post-monsoon and winter) greatly influences the leachability of different heavy metals (Pani et al., 2013). The results of the effect of pH on heavy metals leachability reveal that at low pH of 2 more metals are released from the surface of the fly ash into leachate and as the pH increase the dissolution of metals from fly ash surface decreases (Prasad and Mondal, 2008). Results show that 5-30% toxic elements (As, Cu, Pb, Mg, Al) are leached in a test and around 10% of total Cd was solubilised in the acidic pH range (3 to 5) (Kapoor and Christian, 2016). In general, sorption increases with increasing pH and lower the pH value, the higher the metal released in solution and the more metals are mobilized thus it was concluded that when pH drops to below 5, the mobility is enhanced as a result of the increased proton concentration (Sherene, 2010). The effect of pH of adsorbate on adsorption is studied by varying it in the range of acidic (pH=2) to alkaline (pH=12) and confirmed that removal of heavy metals was highly pH dependent and also the maximum adsorption of Cr(VI), Pb(II), Cu(II) and Zn(II) was observed at the pH value of 8.5, 9.0, 8.2 and 8.3 respectively (Sivakumar and Dheenadayalan, 2012). The leachability of Fe, Cu, Cr and Ni shows of the trend as  $L_{\text{Extraction}} > L_{\text{Buffer}} > L_{\text{Aqueous}}$  in fly ash samples collected from the Indraprastha Power Station, Delhi (Singh et al., 2011). The effect of pH and extraction time on the leachability has indicated that the behavior of trace elements from fly ash is affected by the pH of extraction solution and leaching time (Singh et al., 2014; Tiwari et al., 2015). It was concluded that pH has more influence than the time of leaching in controlling a number of metals leached out from fly ash (Singh et al., 2014).

### **Liquid to Solid (L/S) ratio**

To separate the desired solubilised constituent or to remove a harmful component of the solid phase, the solids are brought into contact with liquids as leaching function. Liquid to Solid (L/S) ratio has an effect on the concentration of the heavy metals or trace elements (Mizerna and Król, 2023) that will leach by the solid into a liquid to which it is exposed (Ibrahim, 2015). Usually the pH of fly ash extracted largely depends on liquid to solid ratio (Ibrahim, 2015) and was confirmed that at lower L/S ratios, higher concentrations of metals were leached (AlAbed et al., 2004) and the concentration of heavy metals decreases with increase in L/S ratio (Gandhi et al., 2013). Leachability increases with an increase in liquid to solid (L/S) ratio (Sivapullaiah and Baig, 2010). In fly ash leachate of liquid to solid ratio (L/S= 0.1 L/kg), the high concentrations of heavy metals Ba, Cr, Cu, Mo, Se, and Zn was reported, while their concentrations decreased as the increased L/S ratio (<http://www.srcosmos.gr/srcosmos/showpub.aspx?aa=13165> –accessed on 30 August 2016). Leachability of As, Cu and, Zn was reported as the highly L/S ratio dependent (AlAbed et al., 2004). In a leaching test, the most of the trace metals have shown its maximum absorption at the lower liquid-solid ratio and then decreases with an increase in liquid-solid ratio (Praharaj et al., 2002). In a serial batch leaching test result from many elements like Mn, Zn, Ca, As, and Mg shows maximum concentration in the leachate at a lower L/S ratio of 4 and 8 (Singh et al., 2010). An increase in L/S ratio decreases the effluent pH and all metal concentrations (Mizerna and Król, 2023; Bestgen et al., 2016).



### Particle size and distribution of metal ions

Indian fly ash is generally fine powder, glassy and particles are spherical in shape (Ram and Mohanty, 2022; Rani and Jain, 2015) and range in size from 0.5 to 150  $\mu\text{m}$  (Sahu, 1999; Kumar, 2005; Siddique, 2007; Senapati, 2011). In general, Fly ash is 80% glassy and 20% crystalline and glassy nature and thus makes it highly reactive (Sahu, 1999). Particle size mostly depends on the fly ash source (Rani and Jain, 2015). According to Basu et al. (2009), the fly-ash particles are empty spheres (cenospheres) filled with smaller amorphous particles and crystals (plerospheres). The surface layer of fly ash particles (microns in thickness) contains a considerable amount of readily leachable toxic elements (Iyer, 2002; Chaudhary and Banerjee, 2007). The release of metals takes place only from those, which are sitting on the surface of fly ash particles (i.e. at adsorbed position) (Sinha, 2005). One of the most prominent features of the fly ash is the gradation effects of particle size on elemental concentration and many researchers (Davison et al., 1974a, b; Klein et al., 1975; Kaakinen et al., 1975) have observed that the decrease in fly ash particle size tends to increase in concentration of As, Cd, Cu, Ca, Mo, Pb, S, Sb, Se, Ti, and Zn (Pandey et al., 2011). Kapoor and Christian (2016) have used fly ash with varying particle sizes from coarse sand to fine silt size (below 3 mm size). The surface analysis has revealed that most heavy metals in fly ash are available within few hundred angstrom depth from the particle surface and therefore vulnerable to easy leaching (Sahu, 1999). In another study (Shivpuri et al., 2011) the mean diameters of fly ash particles were found in the range of 4.2  $\mu\text{m}$  - 207  $\mu\text{m}$ . The fineness of fly ash particles has a decreasing effect on the leachability of traces (Sivapullaiah and Baig, 2010).

### Leaching medium and time

In fly ash leaching tests, many have used deionized water (Sarode et al., 2010; Thomas, 2011; Bhatnagar and Chouhan, 2012 and Pandey, 2014), distilled water (Prasad and Mondal, 2008; Kapoor and Christian, 2016), demineralised water (Goswami and Das, 2006; Badura and Chaudhary, 2016) and rain water (Lokeshappa and Dikshit, 2011) as leachant for release of heavy metals; whereas, Thomas (2011) was used acetic acid. In a batch leaching study, Mg and Cu concentrations show solubility with deionised water and leached in higher concentration in all samples of fly ash (Sarode et al., 2010).

Fly ash leaching and metal mobility is a time dependent experience (Singh, 2013). When fly ash interacts with water the principal process affecting the leaching process are the dissolution of primary solids and precipitation of secondary solids as well as redox conditions, sorption and hydrolysis reactions (Brunori et al., 2001). Leachate quality varies with time and reaches a peak value after a few years and then decline, while all the contaminants don't have a peak value at the same time (Sinha, 2005).

In extraction of Cr and Ni have a relatively higher leachability than aqueous and buffer solution with leaching time, the leachability of Cu is increased in aqueous and extraction solution, whereas, the leachability of Cd increased with leaching time in aqueous and buffer solution and with the increase of leaching time, the leachability of Fe in extraction fluid increased with time with small fluctuation (Singh et al., 2012). Moreover, the effect of contact time between adsorbate and adsorbent is studied by changing it in the range of 15 to 180 minutes and took note that removal of Cr, Pb, Zn and Cu is optimized at the contact time of 60 minutes (Sivakumar and Dheenadayalan, 2012). The leachability of trace element (Fe, Cu, Cr and Ni) in fly ash is affected by time of leaching and also leachability of Pb and Cd fluctuates over time (Singh et al., 2011). The reaction time and atmospheric exposure have a significant impact on the leaching behaviour (Mizerna and Król, 2023) of metals resulted from a WLTs (Bestgen et al., 2016).

### **Mobility and leaching factors of some major heavy metals from Indian fly ash**

**Cadmium:** Cd is a surface-adsorbent element and its mobility depends on sample crystallinity (Rada et al., 2014). It has a little higher leachability with the extraction solution ( $\text{pH} \sim 4.93 \pm 0.05$ ) whereas; the maximum leachability of 0.064 mg/l was achieved in aqueous solution ( $\text{pH} \sim 7$ ), 0.059 mg/l in a buffer solution ( $\text{pH} \sim 10-11$ ) and 0.183 in extraction fluid (Singh et al., 2011). In both batch leaching test and TCLP, cadmium did not leach from the fly ash samples (Sarode et al., 2010) whereas, about 10% of total Cd solubility was reported in a column leaching test with acidic pH (Kapoor and Christian, 2016). The leachability of Cd was found minimum at the beginning and end the of leaching at L/S ratio 20 and 100 in fly ash samples of Chandanpura and Ramagundam (Prasad et al., 2008) also the leachability increases with leaching time in aqueous and buffer solution (Singh et al., 2012). The activities of Cd increased as time increases and pH decreases (Ibrahim, 2015) and it showed maximum mobility in an alkaline solution (Singh et al., 2014a).

**Chromium:** Cr is a highly toxic and carcinogenic heavy metal for all living things (Altıkulaç et al., 2022). In Indian coal fly ash the Cr concentration was generally found lower than other countries, and has higher leachability in aqueous and buffer solutions (Singh et al., 2010). The increase of leaching time increases leachability of Cr in aqueous solution and in buffer solution its leachability firstly increases and after that decreases with increase in leaching time and order was found as  $L_{\text{Extraction}} > L_{\text{Buffer}} > L_{\text{Aqueous}}$  (Singh et al., 2011). Normally, the leachability of Cr was found maximum in an acidic solution (Singh et al., 2014a).

**Copper:** In Indian fly ash, Cu indicated good solubility with deionised water and released in higher concentration in batch test results, while in TCLP test it shows solubility in weak acidic medium and was leached at higher amounts in all samples (Sarode et al., 2010). In addition, with the leaching time, in aqueous and extraction solution the leachability of 'Cu' was increased (Singh et al., 2012). In an experimental analysis, the leachability of Cu with three leachants order was found as  $L_{\text{Extraction}} > L_{\text{Buffer}} > L_{\text{Aqueous}}$  (Singh et al., 2011). Serial batch leaching results Cu concentrations was insignificant in fly ash leachate regardless of liquid to solid (L/S) ratio (Praharaj et al., 2002). The leachability of Cu was found maximum in acidic solution and about 2- 5% of the total Cu is leached at pH around 3 (Singh et al., 2014a). Sometimes, the leachability of copper from fly ash was found as intermittent (Kumar, 2000).

**Iron (Fe):** Fe was found to be more easily absorbed metal of all that was present in fly ash dykes and sometimes the iron leaching was found intermittent from fly ash (Kumar, 2000). Iron oxides showed a lower solubility in deionized water and during a batch leaching, the resulting high pH in the leachates led to a limited removal Fe from fly ash (Sarode et al., 2010). With respect to time and buffer solution, leaching of iron, which rises significantly and fluctuates over time with extraction fluid and aqueous solution and leachability order was found as  $L_{\text{Extraction}} > L_{\text{Buffer}} > L_{\text{Aqueous}}$  (Singh et al., 2011). The leachability of Fe was found maximum at beginning of L/S ratio 20 in fly ash samples of Chandanpura and Ramagundam (Prasad et al., 2008). With an increase in time of leaching, the leachability of 'Fe' in extraction fluid increased with time and showed a little fluctuation (Singh et al., 2012) whereas, in the alkaline solution the leachability of Fe was found maximum (Singh et al., 2014a).

**Magnesium (Mg):** In Indian fly ash, Mg indicated a good solubility in deionised water as leachant and released in higher concentration in batch test results, while in TCLP test it shows solubility in weak acidic medium and was leached at higher amounts in all samples (Sarode et al., 2010). At acidic pH and higher temperature (in MWMP test), magnesium showed significant solubility with water and was leached in higher concentration (Kapoor and Christian, 2016). The leaching of Mg continues for the entire period of leaching (about 2 years) from fly ash (Bokaro Thermal Power Station) and concentrations reduced significantly with time (Kumar, 2000; Singh et al., 2007).

**Manganese (Mn):** Batch test results showed a very low concentration of Mn, while in TCLP test better solubility of Mn was observed even in weak acidic medium and was leached at higher amounts (Sarode et al., 2010). The leachate of fly ash (from Chandrapura) has more manganese concentrations than the leachate of bottom ash, pond ash and weathered ash (Prasad and Mondal, 2009) and it was also noticed that sometimes the manganese leaching was found intermittent (Kumar, 2000).

**Nickel:** This metal has a relatively higher leachability in extraction solution. Increasing of leaching time resulted in the higher leachability of Ni in extraction fluid and a comparable order was found as  $L_{\text{Extraction}} > L_{\text{Buffer}} > L_{\text{Aqueous}}$  with different uses of leachants (Singh et al., 2011). In a batch test nickel did not leach from the fly ash samples (Sarode et al., 2010). The solubility of Ni was reported as noticeably pH sensitive and when pH~1 leachant was used about 10% Ni was removed, whereas, the leachability of Ni was found maximum in an acidic solution (Singh et al., 2014a).

**Lead:** The leaching characteristic of lead is closely associated with mineral characteristics and  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ,  $\text{PbSO}_4$  and  $\text{PbCO}_3$  was considered to be the most important mineral that was involved in leachability of Pb (Singh et al., 2011) and is a highly toxic trace that has caused extensive environmental contamination and health problems (Altıkulaç et al., 2022). Leachability of Pb fluctuates over time and leachant used. In an observation, the leachability of Pb was found slightly higher when the fly ash is mixed with the buffer solution and leachability approaches to a higher value of 0.058 mg/l with an aqueous solution (Sarode et al., 2010). Irrespective of pH and leaching test lead was found to be highly insoluble and almost stationary, while, in an acidic solution leachability was the maximum (Singh et al., 2014a). During the batch leaching, the resulted high pH of leachate led to a limited removal of Pb from fly ash (Sarode et al., 2010). In a serial batch leaching result Pb concentrations was insignificant in leachate, regardless of liquid to solid (L/S) ratio (Praharaj et al., 2002). Sometimes the lead leaching was found intermittent from fly ash (Kumar, 2000) and at low pH = 3 about 72 percent of Pb gets released, whereas at pH = 9 only about 2 % of Pb was leached (Sinha, 2005).

**Zinc (Zn):** In both batch and column tests no Zn leaching was observed from fly ash samples (Sarode et al., 2010) whereas, in meteoric water mobility procedure (MWMP) at acidic pH and higher temperature zinc showed substantial solubility with water and leached in higher concentration (Kapoor and Christian, 2016). At the end of the leaching period (at L/S ratio 100), the fly ash samples of Chandanpura and Ramagundam, Zn showed highest leachability (Prasad et al., 2008). It was reported that the mobility of Zn increases as the time increases (Ibrahim, 2015) and was observed that sometimes zinc leaching was found intermittent from Indian fly ash (Kumar, 2000).

## Conclusion

The following conclusions were drawn on the metal mobility from Indian fly ash:

1. The Indian coal fly ash contains a considerable quantity of SiO<sub>2</sub> with CaO causing alkalinity in the leaching liquid (water) and the high calcium fly ash is more hazardous and is a source of selenium. In a natural environment, the fly ash was alkaline and its pH decreased over time (Ibrahim, 2015).
2. Trace metal concentration in the leachate depends on fly ash weight/solution, pH, and concentration of the elements. The composition of fly ash, types of leachant, L/S ratio, pH, particle size, extraction time and method of leaching test are main influencing factors. The leachability of heavy metals is mainly controlled by their concentrations in the fly ash, in association with fly ash particles, the leachant pH and leaching time.
3. The sequential extraction (SE) procedure facilitate to assess the availability of potential trace and major elements associated with specific fly ash phases under various environmental conditions and thus is advantageous in that way (Ibrahim, 2015).
4. pH is the most influencing factor of heavy metal releases. Leachability of heavy metal is inversely proportional to the pH of the leachate and directly proportional to the leaching duration. In acidic extract, the leaching of trace and major elements increased as the leaching time increased (Ibrahim, 2015).
5. Leachability of heavy metal is low in alkaline nature and thus not correlated to its concentration in ash and whereas maximum mobility can be observed in an acidic pH range of 2 to 3. A general mobility order of heavy metal was observed as Fe>Zn>Ni>Cr>Mn>Cu>Cd>Pb.
6. Rapid leaching of most of the trace metals takes place from the surface of ash particles. A time of 4 hours can be taken as the optimum initial leaching time for water soluble metals in Indian fly ash as in this leaching period most of the metals leach their concentrations more than 90% (Lokeshappa and Dikshit, 2012).
7. Finally, it can be concluded that leachability of heavy metals from the Indian fly ash is mainly dependent on factors including (i) leaching time, (ii) test atmosphere (iii) liquid-to-solid (L/S) ratio (iv) particle size, and above all the initial pH of fly ash and the leachant pH.

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