JOURNAL OF RADIATION RESEARCH AND APPLIED SCIENCES 8 (2015) 523–537

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Suitability of leaching test methods for fly ash and slag: A review

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ARTICLE INFO

Article history:
Received 2 April 2015
Received in revised form
9 June 2015
Accepted 15 June 2015
Available online 2 July 2015

Keywords:
Extraction
Fly ash
Heavy metals
Leaching
Leachate
Slag

ABSTRACT

Fly ash and slag leachate pollution can be of great environmental concern due to generation of these wastes in huge quantities from their respective industrial units, mainly coal-based thermal power plants and iron and steel plants. For simulation of natural leaching in laboratory, various leaching methods are available, but selection of a method that can exactly simulate the real-life scenario for accurate estimation of various pollutants is challenging; particularly, the heavy metals present and impact due to reuse or disposal of these wastes. For choosing the most suitable leaching method according to specific situation, one must primarily consider the chemical and physical properties of wastes, the composition of the source, age of waste disposal, and the climatic conditions of the disposal area. Since these factors may not be specified, a variety of leaching methods with relevant equipment have been proposed by researchers; that are based on their required information to particular conditions in absence of a prescribed protocol and non standardization of equipment. The present review is an attempt to investigate the suitable leaching method for coal fly ash and slag.

1. Introduction

Industrial solid waste leachate pollution is one of the important environmental problems the world faces today. It is an issue that adversely affects the society economically, physically and everyday life of people. The contamination of the water sources and soil due to industrial solid waste leachate is also being linked to some of the diseases that are around currently. It is reported that, frequent ingestion of chromium contaminated water can cause anemia and stomach cancer. Iron ingestion in large quantities results in a condition known as heamochromatosis, where in tissue damage results from iron accumulation (Indian Minerals Yearbook, 2012). In central India, Chhattisgarh is a potential power hub having sufficient mineral resources with surplus energy generation and the largest steel plant in India, which attracts and supports many industries. Natural resources such as water and land are limited and their per capita availability is actually diminishing

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Peer review under responsibility of The Egyptian Society of Radiation Sciences and Applications.
http://dx.doi.org/10.1016/j.jrras.2015.06.003

because of irrational exploitation of natural coal and iron ore resources. The biggest challenge that Chhattisgarh faces is the degradation of environment and natural resources, which is imposing an alarming health hazard.

Lack of efficient industrial solid wastes management, particularly in developing countries like India, has lead to severe environmental problems. Due to limited land for waste disposal, the current practice of uncontrolled dumping of fly ash near industrial belt of towns/cities has created a serious environmental problem due to leachate with presence of various toxic metal and ions (Nalawade, Bholay, & Mule, 2012). It is very important to know the characteristics of the surface water, rain water surrounding the waste disposal sites. The leachate immensely affects the sources of water near to dumpsites. (Singh et al., 2014).

Leachate is the liquid produced when water percolate through any permeable material. It can contain either dissolved or suspended material, or usually both (http://en.wikipedia.org/wiki/Leachate).

Leaching methods are categorized, often based on modes whether the leaching fluid is a single addition (static extraction tests), or is renewed (dynamic tests). Methods can also be classified as batch leaching, in which the sample is placed in a given volume of leachant solution, and as column or flow through systems, and as bulk or flow around systems for monolithic samples (Kim, 2005). Commonly used methods are developed by EPA or promulgated by ASTM.

The Washington State Department of Ecology's (December 2003, Publication No. 03-09-107) report (available online at http://www.ecy.wa.gov/programs/tcp/cleanup.html) indicates that the leaching of contaminants from fill material is a complex process and that the use of leaching test to predict these processes is an evolving area of science. As such, no one single laboratory leaching test can evaluate the leaching behavior of a wide variety of material in a broad range of management scenarios. However, when used within the proper framework, leaching test can provide useful information for environmental decision-making.

A thermal power plant generates large amounts of fly ash which may contain toxic metals and environmental risks associated with these coal fly ashes during wet storage in the ash ponds (Lokeshappa, Dikshit, Giammar, Luo, & Catalano, 2010). The disposal of coal fly ash subjects these metal rich materials to conditions that result in further sequestration of the metals or to their release to the environment (Lokeshappa & Dikshit, 2011). The release and transport of trace metals from coal fly ash material is an area of environmental concern because of the wet storage in the ash ponds. The volatilization, melting, decomposition and the formation of new materials and oxidation are the main mechanisms to transfer the metals from coal to fly ash (Kim, Kazonich, & Dahlberg, 2003). The major potential impacts of fly ash disposal either in ash pond or reused in the cement industry leads to leaching of potentially toxic substances into soils, surface water and groundwater. Environmental concerns regarding the potential contamination of soil, surface and groundwater due to the presence of soluble metal species in the ash pond leachate are of great concern (Praharaj, Powell, Hart, & Tripathy, 2002). The soluble salt content in ashes is closely related to the coal properties and the age of the fly ash and also to the pH and other environmental conditions (Jankowski, Ward, French, Groves, 2006). With respect to leaching, it is important to recognize that coal utilized by products, particularly fly ash, is not a homogenous material. Its elemental and mineralogical composition and its physical properties are a function of the original coal, the combustion temperature and post-combustion cooling rate (Kim, 2002). Volatilization, melting, decomposition, and the formation of new minerals, as well as oxidation, are the mechanisms that transform the minerals in coal (Ann G. Kim).

1.1. *Leaching test methods*

In general, leaching tests can be classified into the following categories (Environment Canada, 1990): (a) tests designed to simulate contaminant release under a specific environmental scenario (e.g., synthetic acid rain leach test or TCLP), (b) sequential chemical extraction tests, or (c) tests which assess fundamental leaching parameters. Many researchers have tried to simulate real-life scenario and suggested various leaching methods justifying the attempts. According to Kosson, van der Sloot, Sanchezand, and Garrabrants (2002) the tests that are designed to simulate release under specific environmental scenarios are limited because they most often do not provide information on release under environmental scenarios different from the one being simulated. This type of limitation has led to widespread misuse and misinterpretation of TCLP results. Reliance on simulation-based testing also results in treatment processes that are designed to “pass the test” rather than to improve waste characteristics or reduce leaching under actual use or disposal scenarios.

Summaries of many of the more commonly used leaching methods have been given by Sorini (1997), Wilson (1995), Kosson et al. (2002), Kim (2003), Hesbach et al. (2005); Menghini, Hornberger, and Dalberto (2005); Hassett, Pflughoeft-Hassett, and Heebink (2005), Kazi, Jamali, Siddiqui, Kazi, Arain, and Afridi (2006), Delay, Lager, Schulz, Horst, Frimmel, and Fritz (2007), Arain, Kazi, Jamali, Jalbani, Afridi, and Baig (2008), Kim and Hesbach (2009), Hesbach, Kim, Abel, and Lamey, (2010), Thorneloe et al. (2013), Kosson and van der Sloot (2014), Kosson, van der Sloot, Garrabrants, and Seignette, (2014), Kalembkiewicz and Sitarz-Palczak (2015). The International Ash Working Group (IAWG) based in Europe has done extensive work on the integration of a variety of tests into a comprehensive leaching system (Eighmy & van der Sloot, 1994; van der Sloot, 1998). Leaching methods are often categorized by whether the leaching fluid is a single addition (static extraction tests) or is renewed (dynamic tests). Various leaching methodologies applicable to a wide variety of waste forms have been reviewed (Garrabrants & Kosson, 2005) where it was noted that release from solid materials is most often estimated using the results of one or more extraction tests designed to measure COPC leaching from materials. Although more than 50 leaching tests have been identified for various purposes and materials, only a limited number address a range of test conditions. That is, most leach tests currently being used are designed to simulate constituent release under a single set of assumptions (EPA/600/R-10/170, November 2010).

Chemical aspects influencing the leaching relate to the fundamental processes controlling the solubility of solids.

These include: (a) the influence of pH on controlling the solubility (b) the influence of dissolved-phase complexing agents, which increase the dissolution and (c) the role of oxidation–reduction potential in increasing solubilization. Chemical aspects can also include reprecipitation or sorption processes, whereby dissolved constituents return to the solid phase (Nordtest Technical Report 539).

It was concluded that the simplest type is leaching is the one-stage leaching procedure. The contact time used in such tests is considered long enough for chemical equilibrium to be established. The main limitation of these tests is due to the lack of information about the temporal behavior of the leachate. This question is solved through the use of leaching column tests. The SGLP (synthetic groundwater leaching procedure) test is particularly adequate for one-stage leaching of fly ash (Georgakopoulos et al., 2002).

Kosson, van der Sloot, Sanchez, and Garrabrants (2002) had proposed framework as an approach to evaluate the leaching potential of wastes over a range of values for parameters that have a significant impact on constituent leaching (e.g., pH, LS, and waste form) and considering the management scenario. This approach presents the potential to estimate leaching much more accurately (than many currently used leach tests), relative to field leaching, when conditions for leach test data are matched with field conditions. The greater accuracy of the proposed approach makes it a useful tool for examining waste and assessing the environmental soundness of a range of waste management options as well as for assessing the effectiveness of proposed waste treatment methods. In addition, the proposed framework provides flexibility to the end user to select the extent of testing based on the level of information needed, and readily permits the incorporation of new testing methods and release models as they are developed for specific applications. Appropriately used in waste regulatory programs, this approach could make those programs substantially more cost-effective and protective of the environment. The flexibility of the proposed approach allows for development of the framework to provide a greater degree of tailoring to site conditions, to account for the effects of other waste leaching parameters critical to a particular site. Reliance on a tiered approach to testing can also make this approach more economical for smaller waste volumes and therefore more broadly feasible.

The national standard referring to waste analysis by leaching test is SR EN 12457 – 2003: Waste characterization. Leaching test is a validation test for granular wastes and sludges. The leaching test standard refers to a liquid/dry solid ratio of 2 L/kg dry solid and 10 L/kg dry solid for 3 types of acid liquid phase: pH about 6 (distillate water), pH about 5 (buffer solution), pH about 3.5 (acetic acid solution). The optimum stirring time is about 4 h. The granular sizes are 4 mm and 10 mm for the waste. After filtration, form liquid phase the specific indicators are analyzed. This standard has been adopted as national standard according to the Environmental Acquis. At European level, the leaching test is available as requirement in German, Dutch or French standards. For these laboratory experiments had been followed SR EN 12457 – 2003: Waste characterization. This standard presents the method for the solubilization of the solid sample, the obtained solution being analyzed by atomic absorption technique. The method is used for solid and plastics wastes, which can be crushed and is not suitable for those wastes for which the leachate volume (aqueous solution) is less than 2l (Matei, Precdescu, Sochaciu, & Berbecaru, 2007).

Leaching Environmental Assessment Framework; a new framework for evaluating leaching of wastes was used for assessing the efficacy of potential treatment processes for mixed wastes (radioactive and hazardous) that contain mercury and the framework is based on measurement of intrinsic leaching properties of the material of concern and using the testing results in conjunction with assumed management scenarios and mass transfer models to estimate release of constituents of potential concern over a defined time period. The framework recommends a collection of four leaching tests that follow the tiered approach of leach testing as published in literature (Kosson et al., 2002). These tests can be used to develop a characteristic leaching profile of the subject material under equilibrium- and mass transfer-controlled release. Each test is designed to vary a critical release-controlling parameter (e.g., pH, liquid-to-solid ratio, leaching time) to provide leaching data over a broad range of test conditions. LEAF is a collection of (a) Four leaching methods, (b) Data management tools, (c) Geochemical speciation and mass transfer modeling, (d) Quality assurance/quality control for materials production and (e) Integrated leaching assessment approaches. LEAF Leaching Methods includes (a) Method 1313 – Liquid–Solid Partitioning as a function of eluate pH using a Parallel Batch Procedure, (b) Method 1314 – Liquid–Solid Partitioning as a Function of Liquid–Solid Ratio (L/S) using an Up-flow Percolation Column Procedure, (c) Method 1315 – Mass Transfer Rates in Monolithic and Compacted Granular Materials using a Semi-dynamic Tank Leaching Procedure and (d) Method 1316 – Liquid–Solid Partitioning as a Function of Liquid–Solid Ratio using a Parallel Batch Procedure. Method 1313 and Method 1316 are applicable for coal combustion fly ash and Method 1313, Method 1316 and Method 1315 for Solidified Waste Analog like blast furnace slag, class C fly ash. A Possible Approach to Beneficial Use Screening Levels has been provided in the form of a flow chart in Fig. 1 (Kosson et al., 2012).

Two Primary Types of Leaching Tests Available Static tests: Short term (minutes to days) and relatively inexpensive. Tests Include both agitated (shake), and passive (non-shake tests) Kinetic tests: Long term (weeks to years) and relatively expensive. The mobility of toxic metals released from wastes is assessed using a variety of risk assessment procedures including the Toxicity Characteristic Leaching Procedure (TCLP), among others (Barna, Sanchez, Moszkowicz, and Méhu, 1997; van der Sloot, 1996; USEPA, 1997). The TCLP test, widely used by state and national agencies, was designed to simulate leaching of heavy metals and organics from industrial wastes to be co-disposed in municipal solid landfills. Over several years, severe limitations of using TCLP in assessing contaminant leaching from industrial wastes such as mine and mineral processing wastes (MPW) have come to light due to its specificity only to landfill conditions and other physicochemical parameters (Al-Abed et al., 2006; USEPA, 1995, 1999).

There are three types of leaching methods: (1) regulatory—those promulgated and approved by a regulatory agency to

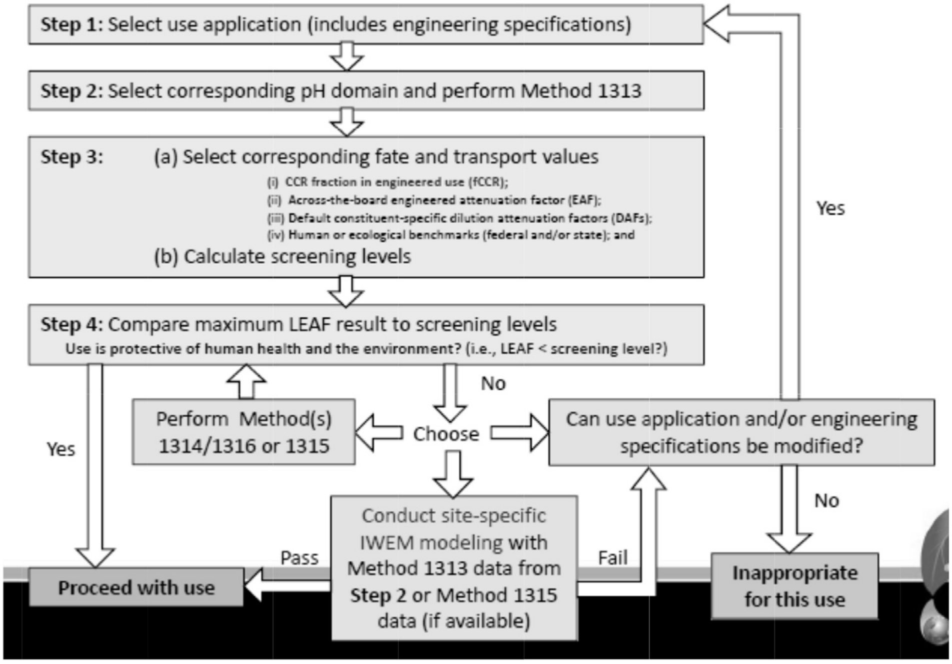

Fig. 1 – **A possible approach to beneficial use screening levels (Kosson et al., 2012).**

generate specific information for submission in a legal context; (2) standard methods are those adopted by a standards organization (ASTM, ISO) for a specific set of conditions and sometimes for specific materials; and (3) research methods developed for a particular objective. Most of this discussion deals with regulatory and standard methods, although examples of some commonly used research methods are included. Regulatory and standard methods are frequently used for research projects. However, results from different projects should be considered comparable only (1) if the method is appropriate to the problem studied; and (2) if the procedure is followed exactly.

1.2. *The column leaching test*

The column test is run in up-flow mode. The leachant is demineralized water (DMW). The test material should have a particle size < 4 mm. Seven eluate fractions are collected within the range of L/S = 0.1–10 L/kg. The total test duration is approximately 21 days. In ISO TC 190/SC7/WG 6 a percolation leaching test similar to CEN/TS 14405 (inorganic) is in development (ISO/AWI 21268-3). This procedure addresses both inorganic and organic contaminants (Hans A. van der Sloot). Column leaching tests are considered as simulating the flow of percolating groundwater through a porous bed of granular material. The flow of the leaching solution may be in either down-flow or up-flow direction and continuous or intermittent. The flow rate is generally accelerated when compared to natural flow conditions. However, it should be slow enough to allow leaching reactions to occur. A basis assumption in column leaching is that the distribution of the leaching solution is uniform and that all particles are exposed equally to the leachant solution. Precipitation or sorption within the column may affect the results. Column experiments more closely approximate the flow conditions, particle size distribution and pore structure, leachant flow, and solute transport found in the field (Zachara & Streile, 1990). Column experiments can be conducted in both saturated and unsaturated conditions. Unsaturated conditions are usually intended to mimic vadose zone placement. Intermittent addition of a given volume of leachant solution at the top of the column can provide uniform distribution of the fluid and approximate a constant fluid front moving through the unsaturated column. Saturated columns are obtained by a constant fluid flux and allowing the fluid to pond at the top of the column. Variables, such as leachate collection, sampling frequency, leachant flow rate, and duration of the experiment are determined by the experimental objectives (Ann G. Kim).

In a report to EPRI (Zachara & Streile, 1990), static (batch) and dynamic (column) methods were compared. Based on a review of the literature, batch systems tend to be inexpensive, simple, and they generate chemical data for mechanistic applications. Column methods are more expensive and more operationally complex, but they generate results that reflect real systems subject to fluid flow and solute transport.

1.3. *Standard test method*

This test method is a standard laboratory procedure for generating aqueous leachate from materials using a column apparatus. It provides a leachate suitable for organic analysis of semi volatile and non-volatile compounds as well as inorganic analyses. The column apparatus is designed and constructed of materials chosen to enhance the leaching of low concentrations of semi volatile and non-volatile organic constituents as well as to maximize the leaching of metallic species from the solid. Analysis of column effluent provides information on the leaching characteristics of material under the conditions used in the test. This test method provides for the passage of an aqueous fluid through materials of known mass in a saturated up-flow mode. It is intended that the sample used in the procedure be physically, chemically, and biologically representative of the material. This test method does not produce results that can be used as the sole basis for (1) engineering design of a disposal site, or (2) the characterization of wastes based on their leaching characteristics. A few limitations of this method; Maximum particle size is 10 mm, not applicable to volatile compounds, not applicable to the characterization of materials that dissolve in water, etc (ASTM D4874-95, 2014).

1.4. *pH dependence leaching test*

This test provides information of the pH sensitivity on the leaching behavior of the material (CEN/TS 14429; CEN/TS 14997; ISO/TS 21268-4; Preliminary EPA Method 1313). The listed methods are very similar in nature and, therefore, it is expected that they lead to very comparable results. The leaching test consists of a number of parallel extractions of a material at liquid-to-solid ratio (L/S) = 10 L/kg during 48 h at a series of pre-set pH values. The pH is adjusted at the start of the experiment with HNO3 or NaOH (or KOH). After 48 h of equilibration by end over-end rotation in PE containers, the suspensions are filtered (0.45 μm) and analyzed. The test provides the response of a material to imposed pH changes and an acid-base titration curve to understand the response of the material to acid or base reactions (i.e. pH buffer capacity) under environmental scenarios (e.g. carbonation, infiltration, sulfur oxidation, soil interfaces) (Hans et al., 2011; Ahmad et al., 2012).

1.5. *Batch leaching test*

Batch leaching methods are those in which a sample is placed in a given volume of leachant solution for a set period of time. Most of these methods require some type of agitation to insure constant contact between the sample and the leachant. At the end of the leaching period, the liquid is removed and analyzed. The most commonly used batch leaching methods are:

- Toxicity Characteristic Leaching Procedure (TCLP),
- Extraction Procedure Toxicity Test (EPTOX),
- Synthetic Precipitation Leaching Procedure (SPLP),
- Standard Test Method for Shake Extraction of Solid Waste with Water (ASTM-D3987), and
- California Waste Extraction Test (WET) (Ann G. Kim).

Batch leaching methods are those in which a sample is placed in a given volume of leachant solution for a set period of time. Most of these methods require some type of agitation to insure constant contact between the sample and the leachant. At the end of the leaching period, the liquid is removed and analyzed. The most commonly used batch leaching methods are the Toxicity Characteristic Leaching Procedure (TCLP), the Extraction Procedure Toxicity Test (EPTOX), the Synthetic Precipitation Leaching Procedure (SPLP), the Standard Test Method for Shake Extraction of Solid Waste with Water (ASTM-D3987), and the California Waste Extraction Test (CA WET). The Leachate Extraction Procedure approved by the Canadian General Standards Board (CGSB, 1987) and the Leachate Extraction Procedure (LEP, 1993) of Ontario are very similar to EPTOX (A. G. Kim).

In the batch leaching this is the sample for a given volume of leachant solution, as column or flow through systems, and as bulk or flow around systems for monolithic samples. Results are generally reported as a concentration, sometimes as the concentration in the leachant solution (mg/L) or as the leached concentration from the solid (mg/kg). In many methods, the liquid to solid ratio (L/S) is used to quantify the volume of leachant with respect to the amount of solid sample, usually as mL/g or L/kg (Kim, 2005). It was concluded that the pH-static leaching test proved useful to identify general leaching trends and, in combination with a complex geochemical approach, applicable to assessment of the leaching behavior of ashes from a cobalt recovering process. The highest amounts of metals and major constituents were released under acidic conditions. The leaching results as well as the diffraction data were very similar for both 48-h and 168-h experiments. Despite some differences, researcher assumes that a standard period of 48 h was sufficient to reach equilibrium in the fly ash–water system (Vitkova, 2010).

TCLP and EN 12457-2 batch leaching tests were used to examine the extraction capacity of various species from solid to aqueous phase under different leaching conditions and also showed that the pH of a leaching test is considered as the most significant factor for the extraction capacity of the species present in a solid sample. Toxicity of TCLP eluates was affected by acetic acid, used as extraction solvent, as well as by the ensuing precipitation that took place after eluate pH adjustment to neutral values. Thus, the EN 12457-2 leaching method proved to be more reliable than the TCLP leaching method for fly ash toxicity assessment (Tsiridis, 2006).

In a series of batch leaching tests were conducted in the laboratory. In order to better simulate the natural conditions and susceptibility to release, a lower liquid-to-solid (L/S) ratio was used. The toxicity characteristic leaching procedure (TCLP) requires the use of an extraction fluid made of buffered acidic medium to run the test and a direct acid digestion method was carried out for the determination of heavy metals. The heavy metal concentration was obtained by use of TCLP. In this procedure sodium acetate buffer was used at pH 4.99 (Sarade, 2010). Used the leaching test developed by Van der Sloot et al. (1984) for close approximation of field conditions, so as to improve the prediction of possible environmental effects (Prasad, 2008; Chezom et al., 2013).

An improved leaching test method has been suggested for environmental assessment of coal ash and recycled materials used in construction and results are considered more representatives of actual field conditions than single-point pH tests which have historically been used in evaluating use of CCRs and other secondary materials. Draft Method 1313, 1314, 1315, 1316 and 1316 leaching test methods are applicable to other materials being used in commercial and engineering applications (Thorneloe, 2009). Georgakopoulos et al. (2002) found the simplest type is the one-stage leaching procedure. The contact time used in such tests is considered long enough for chemical equilibrium to be established. The main limitation of these tests is due to the lack of information about the temporal behavior of the leachate. This question is solved through the use of leaching column tests. The SGLP (synthetic groundwater leaching procedure) test is particularly adequate for one-stage leaching of fly ash (Hassett, 1994; Llorens, 1996).

In the leaching column test, purified water was passed through the fly ash (100 g) in a vertical column with an internal diameter of 5 cm and a fillable height of 15 cm. The permeation procedure was controlled with a Gilson Minipuls 2 peristaltic pump (Gilson Medical Electronics, WI). The flow rate of the pump was 2 mL/h throughout the duration of the test, which was about 200 h (5 pore volumes) (Georgakopoulos, 2002). Vageesh et al. (2002) used a column leaching method to assess the leachate composition and heavy metal contamination. Shivpuri (2011) concluded that the maximum leachable quantities of some trace metals present in coal fly ash are computed by a Sequential Extraction Procedure (SEP) and results are compared with values obtained by Toxicity. Characteristics Leaching Procedure (TCLP) and the leaching trends observed for the six fly ash samples by using acetic acid of 2.88 pH, as leaching solution.

Paul used the Mine Water Leaching Procedure (MWLP) (Ziemkiewicz et al., 2003a, 2003b) as laboratory leaching method. This study attempts field verification of the results of a laboratory leaching procedure that uses mine water to sequentially leach coal ash. In addition, we attempted to begin the process of identifying which chemical parameters could be predicted in the laboratory. The Mine Water Leaching Procedure is a sequential leaching procedure that was developed to determine the longterm leaching behavior of industrial wastes in acidic mines environments. The complex hydrology, redox, and geochemical conditions found within the backfills of most surface mines are difficult, if not impossible to reproduce in a laboratory setting. However, preliminary comparisons of MWLP leachates with field leachates indicates that this procedure may be a valuable tool for predicting the overall trend of leaching behavior for CCBs placed in unique acidic environments (Ziemkiewicz et al., 2011).

Morar (2011) has done the leaching study and found a more realistic analysis of metal leaching from fly ash-soil mixtures can be made in CLTs, as the test set-up more closely mimics the field behavior compared to a batch-scale test. However, batch tests are easier to perform and may be preferred to roughly predict the field behavior. It was also observed that the direct comparison between the two tests is not available, and several issues have to be considered before using the scaling factors discussed above in practice. First, the liquid-to-solid (L:S) ratio does not change during the WLTs while the CLTs are conducted with continuous percolation of eluant, causing a constant increase in the L:S ratio (Ogunro & Inyang, 2003).

Second, shorter equilibration times are used for leaching in WLTs compared to the extended periods of leachate collection and analysis for CLTs. Third, the mixing in the batch procedure is more aggressive than in the CLTS, which probably enhances the surface contact between the leaching solution and the solid particulates. This may result in faster leaching rates of the metals and allow equilibrium between the liquid and the solid phase to occur within a shorter period of time. The aggressive agitation may also increase dissolution of mineral components of the tested material and thereby enhance variations in pH and ultimately affect metal leaching behavior. Also no direct correlations between the concentrations measured in the WLTs and CLTs were found, largely due to the differences in the test conditions (e.g., different liquid-to-solid ratios, test durations, and mixing intensity). Among the two approaches studied, scale-up of the WLT results to the column experimental set-up provided a relatively better prediction of the leachable amount in CLTs (Fig. 2).

Murarka (2003) used batch leaching test of the three ammoniated acidic ash samples and the unammoniated ash were extracted in duplicate at liquid-to-solid ratios: 3:1, 9:1, 27:1, and 100:1. Distilled deoinised water was used to conduct all leaching tests in the study. The extraction or equilibration period was 24 h of continuous end-over-end agitation at 30 rpm for all leaching tests. He also found that the presence of ammonia in fly ash does not appear to change the leaching characteristics of aluminum, barium, boron, chromium, copper, sulfate, chloride, and bromide contained in fly ash. Takao (2007) designed a column with an assumption that rain water is the main source of penetrating through the fly ash landfill, as shown below (Fig. 3).

The fly ash was set in the bottom of a plastic pipe and water penetrates by gravity and the pressure of 150 mm or 225 mm head water. Diameter of the pipe was 28 mm or 56 mm. Palumbo (2009) run the leaching experiment in duplicate using columns with different amount of biochar, fly ash and soil. Columns made of 50 mL syringes were set up on ring stand. The bottom of column was lined with glass wool to prevent the solid fractions from flowing through column. Sauer et al. (2011) concluded that in general, CLTs are the preferred method to assess leaching from soil–fly ash mixtures. The lower L:S ratio and laminar flow in a CLT more closely resemble field conditions compared to the aggressive agitation and high L:S ratio in WLT. Consequently, data from CLTs are preferred over data from WLTs when conducting environmental assessments. In WLT 2 L high-density polyethylene (HDPE) bottles (liquid-to-solid were used with (L:S) ratio of 20:1 (mL/g)) and Column Tests were conducted in general conformance with ASTM D4874. Barman (2012) has used the column leaching apparatus; two different layers of contaminated and uncontaminated soils of different height ratios (ratio of depth of contaminated soil to the depth of uncontaminated soil) are taken. Water is poured from an overhead tank at a particular flow rate to the inlet of the soil column for a certain ponding depth over the contaminated soil. Subsequent infiltration causes leaching and the leachates are collected from the bottom of the column (Fig. 4).

Total height of column has 3 different parts as; H_1: Height of the uncontaminated soil layer. H_2: Height of the contaminated soil layer. H: Height of the water layer above the soil layer which may be termed as ponding depth. Ward et al. (2010) has been developed a series of laboratory based leaching test. Two different test protocols were used: a two stage serial batch testing program in which leachate from representative ash sample were allowed to interact separately with relevant rock material under laboratory conditions and a single-stage mixed batch testing program in which 50:50 mixtures of the same rock sample and ash sample were extracted with water following a similar procedure to leaching tests used for the individual ash and rock sample.

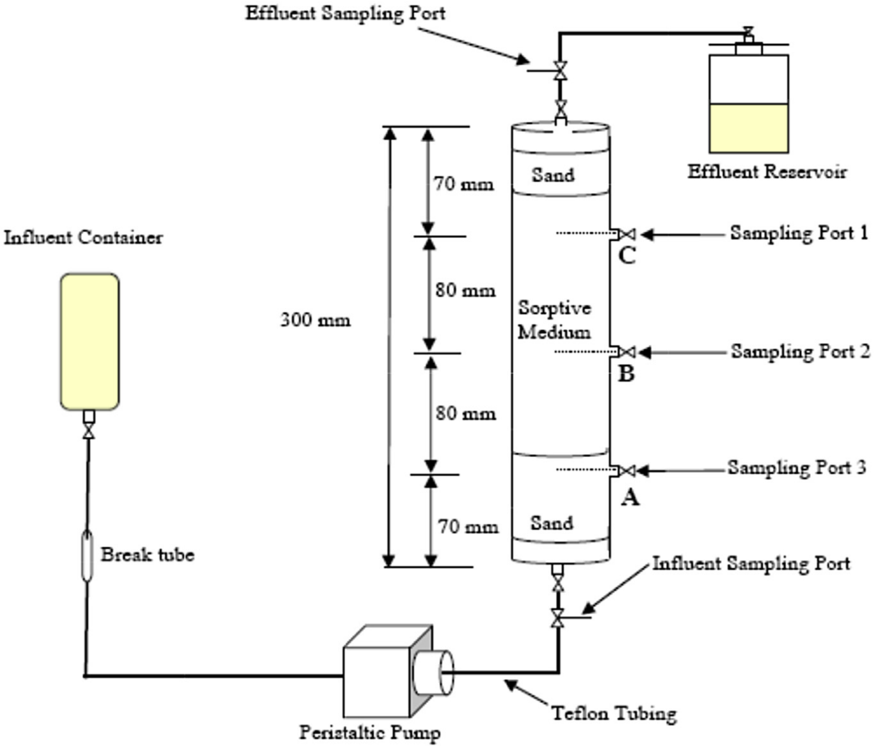

Fig. 2 – Schematic of the column experiment set up (Morar, 2011).

Kazonich et al. (1999) used columns of 1 m section of clear acrylic 2 inch pipe with an approximate volume of 2 L. Threaded PVC pipe caps close each end and have 1/4 inch fittings tapped into them for lixiviant inflow and leachate outflow. Columns are loaded by putting 10 g of glass wool into an empty column and pushing it against the bottom cap. The fly ash is then poured into the column, and another 10 g of glass wool is inserted on top. The top cap is affixed and tightened, and the sealed column is hung vertically from a rack. The column is then connected to the lixiviant delivery

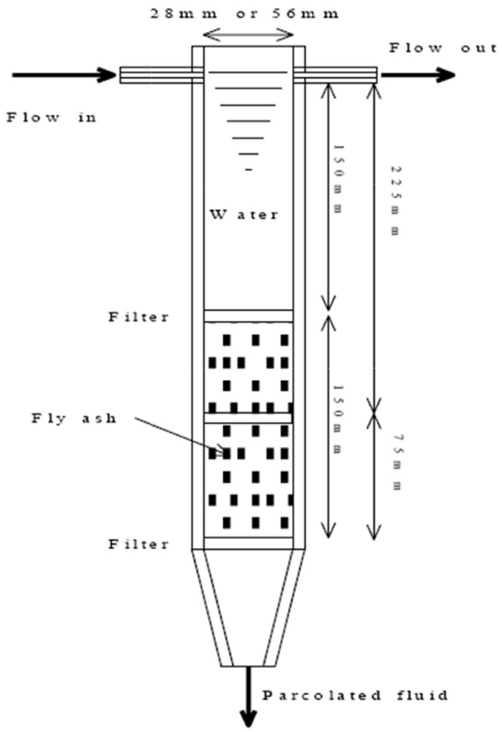

Fig. 3 – Schematic cross section of a test column (Takao, 2007).

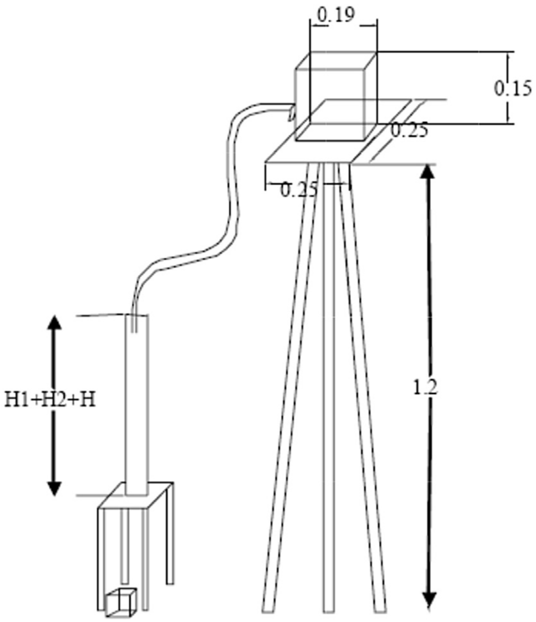

Fig. 4 – Column leach apparatus (all dimensions are in meter) (Barman, 2012).

system. They conclude that the sulfuric and acetic acid leaching results might be considered a worst case scenario.

Leaching tests have been commonly used to predict environmental impact associated with ash disposal (Praharaj et al., 2002). A shake test gives information on the total quantity of an element leachable from ash residue. Due to leaching characteristics of fly ash, the trace elements, along with other constituents, gradually and slowly get leached from the ash and percolate to nearby groundwater. The effect of pH and extraction time on the leachability has indicated that the leaching behavior of trace elements from fly ash is affected by the pH of extraction solution and leaching time. It was observed that when the fly ash was shaken with aqueous solution (pH 7) and extraction fluid (pH 4.93 ± 0.05), the pH of the leachant initially increases, followed by a progressive decrease. The results of the batch shake test, especially with pre-leached fly ash, had shown that the release of elements into extraction medium continues over a period of time. The pH value of leachates obtained during the leaching process appears to be related to the alkalinity of the fresh fly ashes (Singh, Gupta, & Guha, 2012).

After trying to compare our batch leach test to the column study, it was determined that a tremendous amount of work remained to be done. Some of the questions to be answered are: what are the other major constituents in the samples; how did they respond to the same experimental conditions; how are the metals bound to the waste particles; what effect does the change in pH have; what are the solubility limiting factors; does particle abrasion play an important part in the batch test; and will the low application rates give the same type of results. All these questions should be answered before a definite comparison can be made. However, we do feel we can recommend the use of the NBS mixer and a 20/1 liquid-·to·solid ratio for the batch test. A leach time of 12 h would appear to be sufficient, but a 12 h leach test presents a scheduling problem in the laboratory workday; therefore, it may be necessary to use a longer leach time (Jackson, Benedik, & Jackson, 1981; Danielowska, 2006; Demotica et al., 2012; Ecaterina et al., 2007; Jankowski et al., 2006; Kazonich and Kim, 1999; Leaching Methods; National Order no. 876, 2002; NT TECHN REPORT, 2003-10).

It was also reported that the metal concentrations in the TCLP leachate were significantly higher than the metal concentrations in the DWLP leachate. This is due to the pH difference between the applied extraction fluids and also between the final leachate pHs. The pH of the TCLP extraction fluid was around 4.93, but that of the DWLP was around 7.0. Therefore, the TCLP provided more acidic conditions for the waste samples than the DWLP. Moreover, after shaking, the final pH values of the TCLP leachates were within the range 6.05–6.8 and those of the DWLP in the range 8.1–9.5. The pH of the extraction fluids, as expected, affected the final pH of the leachates, and the alkalinity present in the cement also led to higher leachate pH values (Yilmaz, Cokca, & Unlu, 2003).

After using United States Environmental Protection Agency (USEPA's) Toxicity Characteristic Leaching Procedure (TCLP) and USEPA's Synthetic Precipitation Leaching Procedure (SPLP), it is apparent that the leaching of metals in the ferronickel slag is dependent on the extraction fluid and pH, therefore, the leaching and mobility of metals occurring on the environment will also depend for its exposure and usage (Juvelyn et al., 2012) (Tables 1 and 2).

Leaching of activated slag samples is expected to yield results on the long-term stability as well as any change in the leachability of the heavy metals when weathering occurs (Shanmuganathan, Lakshmipathiraj, Srikanth, Nachiappan, & Sumathy, 2008).

Results of TCLP test conducted in the study revealed that leachate concentrations of elements of environmental concern were either undetectable or significantly below the regulatory limits. Noticeable differences were found in test results between TCLP and SPLP for chromium, and lead. Chromium concentrations in SPLP leachates were consistently lower than those in TCLP leachates. Unlike chromium, concentrations of lead leached from most of the tested samples in SPLP leachates were higher than those in TCLP leachates. Leachate concentrations of selenium determined in the study were either around or below the detection limit for both leaching tests. Therefore, no significant difference between TCLP and SPLP could be noted (Shieh, 2001).

The three extraction procedures were used for fly ash, namely, EP, TCLP and ASTM, give different concentrations of elements in extracts of the ash samples The EP procedure gives the highest concentration whereas the ASTM procedure gives the lowest concentration indicating that the extraction results are pH dependent (Baba & Kaya, 2004).

Method 1313: Liquid–Solid Partitioning as a Function of Extract pH using a Parallel Batch Extraction Procedure. Method 1313 describes a leaching extraction procedure for a granular solid material at nine specified pH values used to assess how constituent leaching varies with leachant pH under equilibrium conditions. For many constituents of potential concern (COPCs), solubility and the extent of constituent partitioning into contacting water varies with pH; the pH of leachant in the field may also vary over the range of plausible management (disposal or reuse) options. This test provides information on the intrinsic leaching potential at different pH values, and allows evaluation of leaching potential over the range of plausible field pH values. This method also may be used in conjunction with Method 1314 (Liquid–Solid Partitioning as a Function of Liquid–Solid Ratio) or 1316 (Leaching as a Function of Liquid-to-Solid Ratio) for percolation through granular materials and with Method 1315 (Mass Transfer Rates in Monolithic and Compacted Granular Materials) for mass transfer rate controlled release (i.e., diffusion) from monolithic or compacted granular materials, as needed (http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1313.pdf).

Method 1314 is a percolation column test designed to evaluate the release of constituents from solid materials as a function of cumulative liquid-to-solid ratio (L/S). Granular material is moderately packed into a cylindrical glass column and is contacted by leaching solution at a low flow rate. Solution is introduced in an up-flow pumping mode to minimize air entrainment and flow channeling. Eluate concentrations and cumulative mass releases of constituents of potential concern are plotted as a function of cumulative L/S. Eluate concentrations may be compared to quality control and assessment limits for interpretation of method results (http://www.vanderbilt.edu/leaching/leaching-tests/test-method-1314).

Table 1 – Comparison of leaching test methods used worldwide.

S. no.	Author/year	Location	Method	Equipment	Metals
1	Shivpuri (2011)	India	(TLCP)	–	Fe, Zn, Mn, Ba
2	Palumbo (2009)	Tennessee	Column	Microtox 500 Analyzer	Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fi, Ga, Li, Ni, Pb, Rb, Se, Ag, Si, Ti, V, Zn
3	Sarade (2010)	India	Batch and TLCP	Atomic absorption spectrophotometer,	Zn, Ni, Cu, Fe, Pb, Mn, Mg, and Cd
4	Takao (2007)	Japan	Column	Diagenesis method	Ca, Na, Al, Si, B, Cr
5	Kazonich et al. (1999)	Pittsburgh	Column	–	Al, Ca, Fe, Mg, Mn, K, Na, Sb, As, Ba, Cr, Cu, Pb, Ni, Zn, Be
6	Sauer et al. (2011))	USA	WLT & CLT	–	Cd, Cr, Se, and Ag,
7	Tsiridis (2006)	Greece	TCLP 1311 and EN 12457-2	Photo bacterium *Vibrio fischeri* (Microtox test), the crustacean *Daphnia magna*, and therotifer *Brachionus calyciflorus*	Cr, Cu, Mn, Ni, Pb, and Zn
8	Vítková, Ettler, Hyks, and Astrup (2010)	Zambia	pH-static leaching test	–	Ca, Co, Cu, Zn, Co, K, Mg, S and Si
9	Lokeshappa and Dikshit (2012)	India	Pond	Atomic absorption spectrometry (AAS)	As, Cr, Se and Zn
10	Georgakopoulos (2002)	Greece	SGLP Leaching Leaching Column Test	ICP-MS using Elan 5000	Major (Si, Al, Fe, Ti, Ca, Mg, Na, K, and S) and trace (Ag, As, B, Ba, Be, Bi, Br etc)
11	Vageesh et al. (2002)	India	Leaching Column Test	Atomic absorption spectrometry (AAS)	Cr, Cd, Ni and Pb
12	Arroyo, Fernandez-Pereira, and Coca (2010)	Abroad	Batch	–	As, Mg, Ni, Sb, V, Zn and As
13	Prasad (2008)	India	Cascade method	SEM Photograph, AAS	Fe, Cr, Cd, Mn, Pb, Zn, Cu, Ni and Co
14	Ziemkiewicz	West Virginia	MWLP	–	As, Ag, Be, Cu, Cr, Hg, Mg, Mn, pH, Se, Tl, and V
15	Sushil, and Batra (2006)	North India	Digestion	Atomic absorption spectrometry (AAS)	Cr, Mn, Pb, Zn, Cu, Ni and Co
16	Ward et al. (2010)	Australia	Batch Test	ICP-AES and ICP-MS	Mo, As and Se
17	Thorneloe (2009)	Draft Method 1313, 1314, 1315, 1316 and 1316			
18	Morar (2011)	US	WLT, CLT		Al, As, Cr, and Se
19	Murarka (2003)	Abroad		Atomic absorption spectrometry (AAS)	Al, Ca, Fe, Mg, Mn, K, Na, Sb, As, Ba, Cr, Cu, Pb, Ni, Zn, Be
20	Barman (2012)	Abroad	CLT	Flame photometry	Na, Ca and K

Table 2 – A comparison between conditions used in leaching test methods.

S. no.	Author/year	Method	Diameter	Particle size	L/S ratio	Contact time (h)	Head water/flow rate
1	Shivpuri (2011)	TCLP	NA	NA	1:20	18	NA
2	Palumbo (2009)	Column	50 mL syringes	NA	1:10	48	NA
3	Sarade (2010)	Batch and TLCP	NA	NA	5 and 25	24 and 18	NA
4	Takao (2007)	Column	28 or 56	NA	NA	48–96	150 or 225
5	Kazonich et al. (1999)	Column	2 inch	NA	1:50	30–90 days	250 mL/day
6	Sauer et al. (2011)	WLT and CLT	ASTM D4874	4.8 mm	1:20	18	–
7	Tsiridis (2006)	TCLP and EN 12457-2	NA	NA	1: 20 and 1:10	18 and 24	–
8	Vítková et al. (2010)	CEN/TS 14997	–	pH-static leaching test	10	48 and 168	–
9	Lokeshappa and Dikshit (2012)	Pond/SEP	20 L	NA	1:10	24	10 cm
10	Andreas et al. (2002)	SGLP Column	Polyethylene bottle and 5 cm	NA	1:20 and	18 and 200 h	NA 2 mL/h
11	Vageesh et al. (2002)	Column	NA	NA	NA	12 days	5 cm
12	Arroyo et al. (2010)	Batch	NA	NA	NA	NA	NA
13	Prasad (2008)	Cascade	1 L polyethylene bottle	NA	20–100	18	NA
14	Ziemkiewicz	MWLP	2-L plastic reaction bottles	NA	NA	18	NA
15	Snigdha et al. (2006)	Digestion	Teflon vessel	NA	NA	20 min	NA
16	Thorneloe (2009)	Draft Method 1313, 1314, 1315, 1316 and 1316					
17	Morar (2011)	WLT, CLT	Plastic centrifuge tube, Chromaflex glass columns	Passing the 75-mm sieve	20:1	18	50–60 mL/h
18	Murarka (2003)	Batch	Small mouth bottle	NA	3:1, 9:1. 27:1, 100:1	24	NA
19	Barman (2012)	CLT	NA	NA	NA	NA	50 mL/s, 100 mL/s and 150 mL/s

Table 3 – A comparison of recommended leaching methods for fly ash and slag.

Particulars	TCLP; EPA method 1311	SPLP; EPA method 1312	ASTM D 3987-85	Draft method 1314
Use	To determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.	To determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes.	For leaching of solid waste to obtain an aqueous solution.	To provide the liquid–solid partitioning (LSP) under percolation conditions.
Particle size	9.5 mm	10 mm	As in environment	2.5 mm
Liquid–solid ratio	20: 1	20: 1	20:1/4:1	10:1
Leaching time	18 h	18 h	18 h	21 ± 3 h
Filtration	0.6–0.8 μm membrane filter	0.6–0.8 μm glass fiber filter.	Borosilicate glass or stainless steel funnel	0.45-μm filtration membrane
Agitation	End-over-end shaking speed: 30 ± 2 rpm	Rotary extractor speed: 30 ± 2 rpm	Agitator apparatus, 29 rpm	–
pH	Fluid 1: 4.93 ± 0.05 Fluid 2: 2.88 ± 0.05	4.2	pH 2.88 or 4.93	$2 \le pH \le 13$
Leaching fluid	0.1 N acetic acid solution, pH 2.9, for alkaline wastes 0.1 N sodium acetate Buffer solution	Acetic acid mixture, nitric and sulfuric acids	ASTM Type IV reagent water	DI water or 1 mM $CaCl_2$

Table 4 – A comparison of leaching methods (Hesbach et al.).

Mine Water Leaching Procedure	(Paul F. Ziemkiewicz, Jennifer S. Simmons, West Virginia Water Research Institute National Mine Land Reclamation Center; Anna S. Knox, Savannah River Ecology Laboratory University of Georgia)	To evaluates behavior of an ash in a replenishing acidic media, such as acid mine drainage.	100 g sample, 2 L mine water or 0.002 N H_2SO_4, liquid to solid ratio (L/S) = 20,	End-over-end mixing, 30 rpm for 18 h, filter at 0.7 μm, Measure pH and analyze leachate	Add fresh liquid to solids and repeat until leachate pH is equal to 3.
Serial Batch Leaching Procedure	(Peter A. Hesbach, Steven C. Lamey, National Energy Technology Laboratory)	A rapid screening procedure most applicable for granular material in an environment where there is replenishment of the leaching media.	Availability (alkaline ash) – 9 g sample, 450 mL DI H_2O, L/S = 50	Magnetic stirring, 250 rpm, uncontrolled pH for 2 h, filter at 0.45 μm, Measure pH and analyze leachate,	Add fresh liquid to solids, control pH at 8 with HNO_3, stir 3 h, filter, Repeat, controlling pH at 4 for 2 h, filter Repeat, controlling pH at 2 for 2 h.
Synthetic Groundwater Leaching Procedure and Long Term Leaching	(David J. Hassett, University of North Dakota Energy & Environmental Research Center)	Developed as a simulation of actual field conditions, and addresses the incorporation of species into insoluble molecular matrices in a more static and arid environment.	100 g sample, 2 L DI H_2O, L/S = 20,	End-over-end, 30 rpm, 18 h, filter at 0.45 μm,	Measure pH and analyze leachate, Repeat above for 30 and 60 days
Tier Leaching Protocol	(D.S. Kosson, H.A. van der Sloot, F. Sanchez, and A.C. Garrabrants)	An extensive examination of factors affecting leaching behavior.	Titration curve pretest – 8 g sample, 800 mL DI H_2O, pH 2–12. Availability – titration curve, pH 5–9, 8 g sample, 800 mL 0.5 M EDTA, L/S = 100, pH 7, 7.5, 8.	NA	NA
			Leachability A – 40 g sample, 400 mL DI H_2O, L/S = 10, Adjusted for target final pH, each pH unit 3–12 plus natural pH, 11 samples. Leachability B – DI H_2O, 40 g, L/S = 10; 40 g, L/S = 5; 50 g, L/S = 2; 100 g, L/S = 1; 200 g, L/S = 0.5.	For avail. L-A, L-B – end-over-end, 28 rpm, 48 h,	Filter at 0.45 μm, measure pH and analyze leachates.
Toxicity Characteristic Leaching Procedure	(EPA Method 1311)	Provides leaching data on material as would occur with co-disposal in a municipal waste landfill.	pH test, then 100 g sample, 2 L leaching fluid (acetic acid or acetate buffer)	End-over-end, 30 rpm, 18 h,	Measure pH and analyze leachate.

The concentrations of constituents in the collected eluates are used to derive the cumulative mass release from the column. Both eluate concentration and cumulative release are reported as a function of L/S and may be used as test outputs for assessment purposes. Method 1315 is a semi-dynamic tank leaching procedure used to determine the rate of mass transport from monolithic materials (e.g., concrete materials, bricks, tiles) and compacted granular materials (e.g., soils, sediments, fly ash) as a function of time. Test samples are leached in a series of nine deionized water tanks for specified interval durations. Although the direct method result is eluate concentrations, the test outputs for Method 1315 include the mean interval flux during each test interval and the cumulative mass released through the end of a leaching interval as derived from the eluate concentration and other test information (Garrabrants et al., 2012).

Method 1316: Liquid–Solid Partitioning as a Function of Liquid–Solid Ratio using a Parallel Batch Extraction Procedure. Method 1316 describes a leaching extraction procedure for a granular solid material at five specified liquid-to-solid ratio (L/S) values used to assess how constituent leaching varies with the relative leachant volume in contact with a solid material under equilibrium conditions, and at the pH generated by the test material. Assessment of leaching over L/S of 0.5–10 mL/g-dry provides estimates of initial leachate and pore water composition, as well as cumulative release up to L/S of 10 mL/g-dry for constituents of potential concern (COPCs). The L/S of 10 mL/g-dry parameter is common with the L/S of the Method 1313 (Liquid–Solid Partitioning as a Function of Extract pH) extractions. The method also allows identification of the mode of leaching for constituents (wash out of highly soluble salts or solubility limited leaching) and estimation of constituent depletion by leaching. The results of Method 1314 (Liquid–Solid Partitioning as a Function of Liquid–solid Ratio) provide more reliable initial leaching concentration source term data for groundwater fate and transport modeling. This method also may be used in conjunction with Method 1313 (Leaching as a Function of Eluate pH) and with Method 1315 (Mass Transfer Rates in Monolithic and Compacted Granular Materials) for mass transfer rate controlled release (i.e., diffusion) from monolithic or compacted granular materials, as needed (http://www.cresp.org) (Tables 3 and 4).

2. Conclusion and recommendation

Selecting an appropriate leachate test can be summarized in the following four steps (http://www.epa.gov/waste/nonhaz/industrial/guide/pdf/chap2.pdf):

1. Assess the physical state of the waste using process knowledge.
2. Assess the environment in which the waste will be placed.
3. Consult with your state and/or local regulatory agency.
4. Select an appropriate leachate test based on the above information (Table 5).

Kim and Hesbach (2009) conducted a comparison of five leaching techniques and found that cumulative elemental release by weight of sample was lower for the procedures conducted under alkaline (SGLP) to mildly acidic (TCLP) conditions (Brubaker et al., 2013). Many leaching tests used to evaluate the environmental impact of fly ash use have the limitation of not considering the hydrogeologic setting. These tests consider the use of by-products in bulk form, but not in mixtures (Bin Shafique, Benson, & Edil 2002). For example, use of fly ash in Wisconsin is regulated by Ch. NR 538 of the Wisconsin Administrative Code. This regulation requires water leaching tests (WLT) of fly ash in bulk form, but does not consider mixtures, such as fly ash stabilized soil. In addition, WLT does not necessarily model leachate produced in the field. The WLT indicates the potential for contaminant release from fly ash or mixtures, but does not evaluate how a fly ash or fly ash mixture will impact groundwater (Bin-Shafique et al., 2002).

Leaching of heavy metals from the dumped fly ash and steel slag may have negative impact on the environment should be reduced by leaching assessment of these wastes. So, leaching test is one important aspect in the environmental assessment of the remedial measures of solidified and stabilized (S/S) contaminated sediments. Selection of an appropriate test or combination of tests is of vital importance for the proper judgment of results, as well as for predicting the long term release of S/S contaminants into the environment (Aranda, 2008). Metal concentrations in the TCLP leachate were significantly higher than the metal concentrations in the DWLP leachate (Yilmaz et al., 2003).

The main factors that influence the selection of a suitable leaching method for fly ash and steel slag are: Climatic condition of the area, rainfall data, Water head and flow rate to simulate the real dump situation.

Empty Bed Contact time, Particle size as we all know that the particle size is directly proportional to contact area, is necessary it is necessary to consider the particle size for the worst leaching condition. Liquid to solid ratio, Bed density/porosity/void ratio are also playing an important role in leaching operations.

The pH is the most important parameter for any leaching method; it is clear from literature review that the maximum amount of heavy metals gets released under acidic

Table 5 – Conditions of leaching tests (Kalembkiewicz, & Sitarz-Palczak, 2015)

Tests conditions	USEPA [USEPA 1987]	TCLP [TCLP 1311 1990]	ASTM D 3987-85 [2001]
Leaching solution	0.5 mol/dm^{-3} Nitric acid	2.5% Acetic acid	Distilled water
Liquid to solid ratio [cm^3/g]	20:1	20:1	20:1
Leaching time [h]	24	24	24
pH of leaching solutions	0.6 ± 0.1	4.0 ± 0.1	6.3 ± 0.1
Temperature [°C]	19–25	19–25	19–25
Number extraction	1	1	1

environment. The initial pH of the waste sample should also be considered for during final leaching experimentation.

Takao (2007) designed a column with an assumption that rain water is the main source of penetrating through the fly ash landfill.

The ASTM E 50.03 committee is currently developing a standard guide or procedure to identify the best available leaching tests for specific materials or material types (Pflughoeft-Hassett, 2004). In the absence of an accepted protocol, the project objective and the type of data desired determine what method is most appropriate (Ann G. Kim). Numerous leaching studies of coal fly ash have demonstrated that the quantity of major and trace elements extracted can be extremely variable, depending on the nature of both the fly ash and the leaching solution (Brubaker et al., 2013; Van Der Sloot et al., 2011., Valerie, 2007). It is difficult for a new researcher to identify the suitable leaching method for fly ash and steel slag according to their particular situation of the study area. It is observed from literature review the widely used and suitable leaching methods for fly ash and steel slag are: Toxicity Characteristic Leaching Procedure (TCLP), Column leaching test and Batch leaching test through which real field situation can be correlated. Also it is recommended that, all the above discussed factors along with real field conditions are needed to be given due attention in selection of a leaching test for fly ash and slag.

Acknowledgement

This research paper is made possible through the help and support from everyone, including: my PhD supervisors, family, friends, and in essence, all sentient beings.

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