

## Proposal for a Joint Research Program

### Environmental Assessment of Coal Ash Leaching Properties and Beneficial Use Applications using the Leaching Environmental Assessment Framework (LEAF)

#### TASK 2 – DEFINING PHYSICAL-CHEMICAL LIMITS IN USE OF FLY ASH IN INFRASTRUCTURE APPLICATIONS

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September 2017

## **ABSTRACT**

The use of coal fly ash in Israel spans various application fields including infrastructure, construction and agriculture depending on its definition as "usable ash" from the perspective of environmental safety. One of the main potential uses of fly ash in infrastructure works involves the use of fly ash as a fill material in road and railroad embankments.

From previous studies conducted in Israel and worldwide, it is known that trace element leaching depends strongly on the pH level and liquid-solid ratios. In the various applications in which fly ashes are utilized, the fly ash comes in contact or is blended with other substances which could influence its characteristics. The basic approach of this research proposal is to understand the fly ash "as is" and in mixtures in order to estimate the actual contamination potential subject to varied environmental conditions. Geochemical speciation-based equilibrium and mass transport modeling will be used to extrapolate performance to a wider range of fly ash types, external influences and application scenarios. This proposal also builds on knowledge already gained through the Israeli National Coal Ash Board (NCAB) research with respect to the composition and leaching properties of specific Israeli fly ashes.

The proposed research, "Defining physical-chemical limits in use of fly ash in infrastructure applications" will focus on characterizing the leachability of constituents of potential concern (COPCs) in typical infrastructure application containing fly ash.

The overall goal of this project is to develop and demonstrate a methodology for evaluating the environmental acceptability of the use of coal fly ash in Israeli infrastructure projects. Bounding example cases (e.g., using fly ash with upper levels of elemental COPCs) will be used as the demonstration basis for this project such that if shown to be acceptable, the majority of fly ashes potentially to be used in Israel also would be suitable for use.

The specific objectives of this project in order of importance:

1. Characterizing elemental leachability from relevant cementitious mixtures containing fly ash.
2. Depicting elemental leachability dependence on processing quality of fly ash used "as is" as fill material in infrastructure projects.
3. Use of fly ash to improve soil properties in infrastructure.

Currently, the project is emphasizing only on the first two objectives.

Objective 1 is an expansion of previous CLSM and grout research that was carried out on cementitious mixtures with relatively high fly ash content. The main focus in this part will be on comparison, modeling and necessary complementing analysis.

Objective 2 is evaluating the use of fly ash “as is” in Infrastructure. A typical infrastructure use is embankment filling undertaken by compaction of fly ash (with ~10% water). With time, the fly ash is susceptible to natural cycles of wetting and drying. As part of Objective 2, the aim is to prepare and examine fly ash samples in conditions similar to the material life cycle in the infrastructure application. The samples will be tested by the US EPA leaching tests (i.e., Methods 1313, 1314 and 1315) at the different stages of sample progress from loose fly ash through to the final monolith product that has undergone aging under designated conditions.

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## INTRODUCTION

The use of coal ash in Israel in general and fly ash (FA) in particular spans various application fields including infrastructure, construction and agriculture depending on its definition as "usable ash" from the perspective of environmental safety. The criterion of meeting environmental safety is in addition to the ash or ash-derived material meeting appropriate physical or engineering requirements and providing tangible benefits through the designated use. This criterion is application dependent and can be determined by evaluating the environmental impact of the FA use such as the extent of metal leaching under specific application scenarios. The approach taken here is to evaluate "bounding" or "worst case scenarios" such that use conditions found to be acceptable would require minimal further testing for use of a broader set of FA in similar applications.

One of the main potential uses of FA in infrastructure works involves the introduction of FA as a fill material in road and railroad embankments. This type of use is especially beneficial in cases where the underlying layers are wet clayey soils which tend to consolidate under the expected embankment load. The relatively low dry density of the compacted FA may help to lower settlements during the service life of such embankments. An example of such a use is the Jasar A Zarka project constructed in Israel in 1998. In addition, the FA when used "as is" (without blending it with other materials) may serve as a good fill material in other embankments due to its low permeability and its inactivity compared to clayey soils. A number of such projects were constructed in Israel, mainly around the years 1998-2005, when FA was offered in the market at very low cost.

From previous studies conducted in Israel (Teutsch and Berlin, 2015a; van der Sloot, 2009) and worldwide (Adriano et al., 1980; Hjelmar, 1990; Kosson et al., 2009; van der Sloot et al., 2010), it is known that trace element leaching depends strongly on the pH level and liquid-solid ratios. For most elements, solubility is higher at low pH (acidic conditions) than at high pH (basic conditions). However, several elements such as antimony, arsenic, molybdenum and selenium display an inverse response, and hence their solubility increases with increasing pH or reaches a maximum at slightly alkaline conditions (e.g., pH 7 – 9). In the various applications in which FAs are utilized, the FA comes in contact or is blended with other substances which could influence its characteristics, such as cement in concrete mix (Garrabrants et al., 2014; Kosson et al., 2014a; van der Sloot et al., 2012) or soils (Tastan et al., 2011) and other materials in agricultural application and infrastructure construction (Schreurs et al., 2000; Spee and Reintjes, 1986). Therefore, FA characterization (e.g., chemical composition and leaching properties) alone is not sufficient in characterizing FA for environmental applications. For example, when FA is added to cementitious mixtures, the leaching characteristics of the resultant material often are controlled by the cement chemistry (rather than the ash chemistry) and could be different

than the component materials. Consequently, the basic approach of this research proposal is to understand the FA mixtures as a whole and by studying the raw materials (total content and leachability properties), including the FA used in addition to typical blended mixtures of the various applications. In this way, it will be possible to estimate the actual contamination potential subject to varied environmental conditions. Geochemical speciation-based equilibrium and mass transport modeling will be used to extrapolate performance to a wider range of FA types and application scenarios (Kosson et al., 2014b; van der Sloot, 2003; van der Sloot, 2009; van der Sloot et al., 2010). This proposal also builds on knowledge already gained through the Israeli National Coal Ash Board (NCAB) research with respect to the composition and leaching properties of specific Israeli FAs.

Over 20 years of collaboration between United States and European research teams in the field of leaching, environmental assessment, and test standardization resulted in the joint scheme “Leaching Environmental Assessment Framework” (LEAF). The framework recommends a collection of four leaching tests that follow the tiered approach of leach testing as published in literature (Kosson et al., 2014b; Kosson et al., 2002) with applicability to a wide range of materials and uses. A premier achievement of LEAF was an extensive documentation of the technical basis (Garrabrants et al., 2010) and interlaboratory validation process of four new United States Environmental Protection Agency (EPA) methods that resulted in common practice characterization tests of wastes in general and FA in particular (Garrabrants et al., 2012b; Garrabrants et al., 2012c). Analogous test methods are available in Europe through the European Committee for Standardization (CEN) for use in evaluation of waste, soil, sludge and construction products (van der Sloot, 2003; van der Sloot et al., 2008). 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.

From previous work (Kosson et al., 2014b), the distinction between highly soluble substances (readily quickly released) versus solubility limited substances (release limited by mineral dissolution) proved crucial in understanding long term release behaviour. In the latter case, the release is affected by external processes that can alter pH (e.g., by carbonation), changes in redox state (e.g., by oxidation), or change in mobility due to complexation with dissolved organic carbon (e.g., released from overlying layers containing natural organic matter). The pH dependence and the associated geochemical modelling proved valuable tools in recognizing and subsequently assessing the impact of such changes (Kosson et al., 2014a; Kosson et al., 2014b).

From studies on different FAs, it was observed that to a large extent the same mineral set can be used to describe release behaviour from different FAs. This is indicative of the fact that the same mineral and sorptive phases control release from a coal FA matrix and the

available content of different elements in ashes lead to a specific solid-liquid partitioning (SLP) behaviour.

Primary constituents of potential concern (COPCs) with respect to coal combustion products (CCPs) include antimony (Sb), arsenic (As), boron (B), cadmium (Cd), chromium (Cr), lead (Pb), lithium (Li) mercury (Hg), molybdenum (Mo), selenium (Se), and vanadium (V). Boron, As, Li and Mo are of particular concern with respect to surface impoundments while As, and its association with calcium content, is especially important with respect to landfills (US EPA, 2014). However, other primary constituents of CCPs that provide the basic mineralogy and geochemical conditions include aluminum (Al), barium (Ba), calcium (Ca), iron (Fe), sulfur (S as sulfate or sulfides), phosphorous (P as phosphate), chloride (Cl), bromide (Br), organic carbon (OC), and carbonate. The speciation of these elements is particularly important to capture in geochemical conditions because it influences the release of COPCs under field conditions (Kosson et al., 2014b; Roy and Berger, 2011). Specific elements may be of greater concern at some locations. For example, considerable controversy and subsequent research effort has focused on the behavior of Se in response to the coal ash release at Kingston, TN (for example, see (Schwartz et al., 2016)).

The factors that impact the leaching of constituents from CCPs include the coal type burned, the presence of residual un-combusted carbon, and process additives used to improve CCP collection, flue gas conditioning and residue properties (e.g., sulfuric acid to improve ESP performance, bromine addition to improve mercury capture, ammonia addition to reduce NO<sub>x</sub> emissions, trona addition for removal of sulfur and carbon from flue gases).

The following are a few important examples of how additives can significantly impact the geochemistry and leaching behavior of the CCPs:

- Use of sulfuric acid spray to improve FA collection by electrostatic precipitates (ESP) forms in an acidic coating on FA which can result in initially low leachate pH (e.g., pH 3), elevated concentrations of COPCs and wash off of elevated sulfate concentration (Garrabrants et al., 2012a).
- Addition of calcium bromide to coal during combustion results in higher bromide content in initial FA leachate, along with the potential for higher COPCs concentrations through aqueous complexation (Dombrowski et al., 2008); data in preparation for publication).
- Addition of ammonia for selective catalytic and non-catalytic reduction (SCR, SNCR) of NO<sub>x</sub> can result in elevated concentrations of ammonia in leachate leading to increased leaching of mercury and arsenic (Wang et al., 2006; Wang et al., 2007).

For most CCP management scenarios, local equilibrium within CCP pore water is a reasonable assumption for first order modeling and approximations. However, large-scale

field conditions are subject to preferential flow pathways within the CCPs and strong gradients (e.g., oxygen, carbon dioxide, ionic strength) can be present near interfaces at fill boundaries that can influence observed leachate characteristics. Thus, the general approach proposed here is to (i) define representative scenarios and parameter ranges (i.e., conceptual models) that impact leachate composition and quantity, (ii) develop multi-constituent geochemical speciation equilibrium models that can be used to understand the effects of CCP types, blends, and conditions (pH, redox, additives, iron and organic content), (iii) develop hydrologic models for the scenarios to assess water balances, local flow conditions and influence of preferential flow), and (iv) integrate geochemistry and hydraulic information into reactive transport models. Previous research has shown that relatively simple reactive transport models (such as dual regime percolation, and flow around monoliths) can provide a useful basis for decisions (Kosson et al., 2014b; van der Sloot et al., 2017; Verschoor et al., 2008).

The four leaching tests contained within LEAF:

- **Method 1313:** Liquid-Solid Partitioning (LSP) as a Function of Eluate pH Using a Parallel Batch Extraction Procedure
- **Method 1314:** Liquid-Solid Partitioning (LSP) as a Function of Liquid-to-Solid Ratio Using an Up-Flow Percolation Column Procedure
- **Method 1315:** Mass Transfer Rates in Monolithic and Compacted Granular Materials Using a Semi-dynamic Tank Leaching Procedure
- **Method 1316:** Liquid-Solid Partitioning (LSP) as a Function of Liquid-to-Solid Ratio Using a Parallel Batch Extraction Procedure

LEAF includes the program LeachXS Lite™ for database management, enabling comparisons of leaching data for different tests or materials, including outputting data to Microsoft Excel®. LeachXS Lite is available for free licensing and is based on the LeachXS™ platform. The full-featured software in LeachXS Pro allows for advanced modeling and data management capabilities, beyond the features included in LeachXS Lite, and is licensed for an annual fee.

The results of the LEAF tests can be used empirically or in combination with chemical speciation and scenario-specific mass transport models to estimate constituent leaching for a wide range of application scenarios. Application- and scenario-specific evaluations that consider regional or local geographic conditions (i.e., precipitation, hydrology, soil types, etc.) then can be used to establish decision or acceptability criteria for on-going use of ash based on simplified LEAF testing. EPA in collaboration with VU and HvdS has carried out extensive leaching characterization of FA (Kosson et al., 2009) and FA derived products (van der Sloot et al., 2012) and is currently developing guidance on the use of LEAF as the basis for environmental safety criteria for use of FA and other coal combustion residues in a range of applications.

## PROJECT GOAL AND OBJECTIVES

The overall goal of this project is to develop and demonstrate a methodology for evaluating the environmental acceptability of the use of coal FA in Israeli infrastructure projects. Bounding example cases (e.g., using FA with upper levels of elemental COPCs) will be used as the demonstration basis for this project such that if shown to be acceptable, the majority of FAs potentially to be used in Israel also would be suitable for use.

The specific objectives of this project in order of importance:

1. Use in Cementitious Mixtures. Characterizing elemental leachability from relevant cementitious mixtures containing FA.  
Evaluating the effect of high FA content in concrete and cementitious materials to understand the upper bounds for potential usage rates.
2. Use of Fly Ash “as is” in Infrastructure. Depicting elemental leachability dependence on processing quality of FA used "as is" as fill material in infrastructure projects. Tracking changes in leachability characteristics and mechanical properties as a function of compaction procedures and conditions, time and conditions during the progressive strengthening from compacted FA to monolithic behavior.
3. Use of Fly Ash to Improve Soil Properties in Infrastructure. Examining the use of FA as part of a mixture, for uses such as the stabilization of clay soils with FA, to be used as subgrade layers or as embankment fill material in infrastructure projects.

At this point, the project is emphasizing only on the first two objectives.

## METHODOLOGY

1. Use in Cementitious Mixtures. The first topic is an expansion of previous CLSM and grout research that was carried out on cementitious mixtures with relatively high FA content. These mixtures can be compared with lower FA mixtures studied previously on USA mixtures. The justification for the comparison lies with the high similarity of the Israeli (Colombian CerD FA) and one that was used in the USA study. Hence, the main focus in this part (and consequently finance support) will be on comparison, modeling and necessary complementing analysis (e.g., carbonate content).  
The monolith data produced by GSI on grout and CLSM will be evaluated based on 1313 and 1315 tests. Selected monoliths remaining at GSI will be evaluated for the depth of carbonation and leaching at the Technion. Limited modeling will be carried out by H. van der Sloot and D. Kosson to understand effects of partial carbonation relative to the previously obtained testing results - Method 1313 and 1315 results.
2. Use of Fly Ash “as is” in Infrastructure. The process of embankment filling is undertaken by compaction of the FA with an addition of about ~10% water. With time,

the FA is susceptible to natural cycles of wetting and drying. The preparation of the samples to be studied will follow common field practice and will be tested under different atmospheric environments. The US EPA leaching tests will be the fundamental processes used to evaluate the leaching properties. Method 1313 (pH dependence) will be used to characterize the various materials forming along the path of embankment filling life cycle. Method 1315 (monolith/granular material mass transport) will be applied to track the leaching features of the changes from FA to monolith structure. Method 1314 (percolation through a column) on crushed monolith to characterize the cumulative release under equilibrium conditions of the end product.

3. Use of Fly Ash to Improve Soil Properties in Infrastructure. The third part will focus on mixtures of FA with heavy clayey soils according to blends used for soil stabilization. The methods applied will be similar to part two. Use of previous studied materials including the clay soil used in the agricultural LEAF project will be useful.

## **ANTICIPATED PRODUCTS**

1. A manuscript for a peer-reviewed journal that documents results of grout and CLSM testing and modeling.
2. Recommendations for FA types that can be used for infrastructure base layering including limitation specifics if applicable. The LEAF approach enables evaluation of other FAs types (beyond the studied ones) based on the leaching tests and modelling capabilities within LeachXS.
3. A manuscript for a peer-reviewed journal that documents the results of the physical-chemical characteristics and limits of FA usage in infrastructure base layering.
4. Recommendations for FA types and FA to soil ratios appropriate to apply for thinning of heavy soil for infrastructure embankment filling. These requirements should be appropriate for environmental safety of FA usage including limitation specifics if applicable. As mentioned before, at this point the soil-FA mixtures topic is not included in the present work.
5. All new data from the current task (three sub-tasks) will be added to NCAB/GSI LeachXS appropriate databases.

## **MATERIALS AND METHODS**

### **GROUT AND CLSM**

The cement mixtures of grout and CLSM, which were studied previously (Teutsch and Berlin, 2013; Teutsch and Berlin, 2015b), were prepared with high contents of the Colombian FA CMC-CerD, which was chosen for its high concentration of contaminants and

its low pozzolanic activity (i.e., expected to release the highest contaminants concentration). Mixtures with and without FA were prepared according to Table 1.

Table 1. Composition of CLSM and grout cementitious mixtures (kg)

<b>mixture</b>	<b>fly ash</b>	<b>cement</b>	<b>Sand<sup>2</sup></b>	<b>water</b>	<b>total</b>	<b>Admixture<sup>3</sup></b>
<b>CLSM</b>	400 (20% of the mixture)	120	1250	250	2020	1.0 kg/m <sup>3</sup>
	0	150	1500	300	1950	1.0 kg/m <sup>3</sup>
<b>grout</b>	800 (44% of the mixture)	400	200	400	1800	0
	0	800	650	300	1750	0

<sup>1</sup>An additional empty container with no cube served as procedural blank

<sup>2</sup>fine sand 0-4 mm

<sup>3</sup>air entrained agent

### **FLY ASH**

For the current research the main FA to be studied is La Loma FA, which was used for the agricultural LEAF research and was incorporated into the N-viro soil product. This FA has been characterized for its total content and examined by methods 1313 (pH dependence) and 1314 (percolation column). Data of the 2017 FAs to be examined by the GSI will be used for choosing a suitable second FA. The choice will be based on high leached COCPs during EN-12457-2 (i.e., leaching at natural pH of the material at L/S of 10 for 24 hours), ammonia content and pozzolanic activity. The two chosen FAs should differentiate in their pozzolanic activity. These values are partially affected by the CaO content of the FA and will be compared on a ternary diagram of Si-Al-Ca.

### **SAMPLE PREPARATION**

In this study monolithic and granular material will be tested. Monolithic samples are cut or cored from larger samples or molded to size. Compacted granular samples are compacted using modified Proctor compaction at optimum moisture content. The amount of added water will depend on the analysis of water content and optimal moisture of the FA. The specimen size is subject to a minimum dimension specified to ensure that depletion of COCPs does not occur over the duration of the test (Garrabrants et al., 2010). For producing a representative homogenous monolithic material, the FA will be casted at the Technion into a PVC/plastic cylinder mold with a diameter of ca. 10 cm.

Three levels of compaction will be tested; 91%, 89% and 87% of the Maximum Modified Proctor Density.

The samples will be aged under two types of atmosphere: (1) exposed samples typical of the embankment surface layer in which carbonation occurs and (2) covered samples intact from atmospheric CO<sub>2</sub> representing the inner part of the embankment.

Every effort will be made to ensure stable aging conditions and prevent a change in water content of the samples. The specimens will be aged until the testing age in the laboratory room under normal standard conditions according to the Israeli Standard 26 Part 3 – at the temperature of  $(21\pm 3)^{\circ}\text{C}$  and air relative humidity at least 95%. The water content and initial dry density will be determined in accordance with Test Method D2216 and Test Method D7263, respectively.

These two types of samples will be left for 90 days, 6 months and one year. A schematic chart of the various specimens is presented in figure 1.

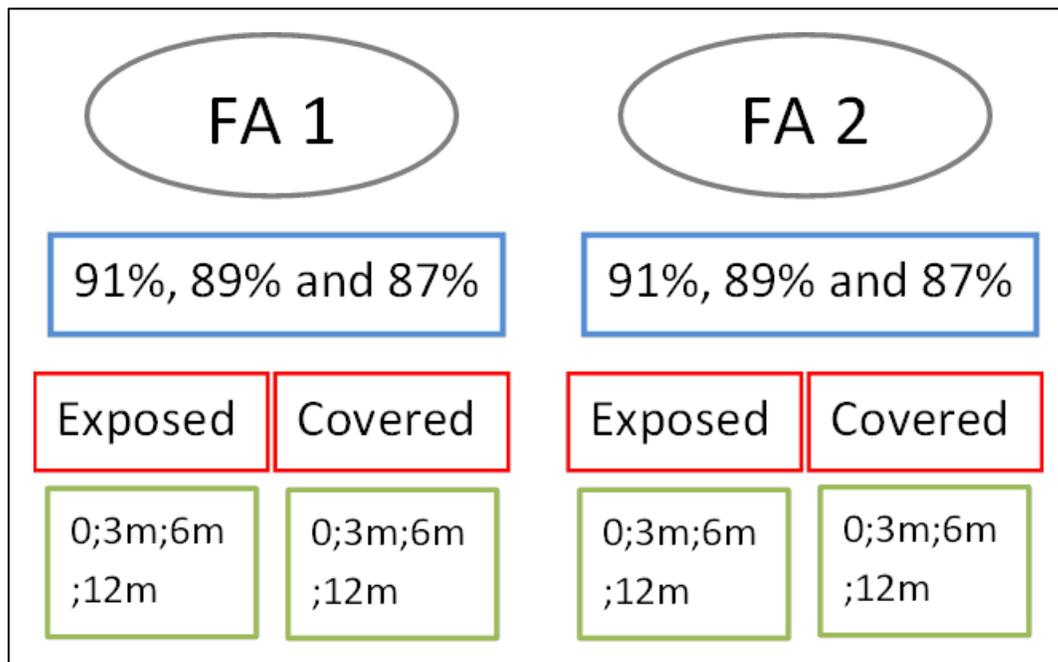


Figure 1. The proposed study specimens: 2 FAs, each at three compaction levels, left to age under exposed or covered conditions and sampled initially, after three months, six months and finally one year.

Method 1313 will be applied to the two initial FAs, and to one level of compaction (e.g., 89%) for each exposure condition after the final aging period (one year). The other compaction levels will be tested by thermo gravimetric analysis (TGA) and the natural pH analysis (EN-12457-2). The initial FA and the final product (one year) will be also tested by Method 1314 similar to Method 1313. Method 1315 will be applied to the compacted granular material for all compaction levels and exposure conditions at the initial and final stages and at the intermediate aging time, only one compacted level (same as for 1313 and 1314) will be tested. All tests will be conducted in duplicate. However, as these variable

conditions result in a large amount of analysis, if possible, further screening will be applied based on initial tests and a reduced number of analyses will be conducted.

#### **METHOD 1313: LIQUID-SOLID PARTITIONING AS A FUNCTION OF ELUATE pH USING A PARALLEL BATCH EXTRACTION PROCEDURE**

Method 1313 is an equilibrium-based leaching test designed to provide eluate solutions representing the liquid-solid partitioning (LSP) curve of constituents as a function of eluate pH (Garrabrants et al., 2012c). Method 1313 is equivalent to EN 14429 and EN14997. The procedure consists of nine parallel batch extractions at targeted pH values and one extraction at the natural pH of the material. The natural pH (also referred to as “own pH”) is the final eluate pH response of a deionized water extraction of a solid material

(i.e., no acid or base added) conducted at an L/S 10 mL/g-dry. The solid material may require particle size reduction by crushing in order to facilitate the approach to solid-liquid equilibrium within a reasonable extraction timeframe. Dilute acid or base in deionized water is added to each extraction according to a pre-test titration in order to achieve final extract pH values at specified target values ranging between 2 and 13 at an L/S of 10 mL/g-dry. The extraction contact time ranges from 24 to 72 hours based on the grain size of the “as tested” material (i.e., the material after any particle size reduction or air drying required to improve the handling of the “as received” material). The pH and conductivity of the final extract solution are recorded and vacuum- or pressure-assisted filtration is used to separate the liquid and solid phases prior to chemical analysis of the eluate. Eluate concentrations for constituents of interest are plotted as a function of eluate pH allowing for comparison to quality control and assessment limits. Eluate concentrations may also be interpolated to the target pH values to provide a uniform basis for comparison of results as the recorded eluate pH is likely to differ slightly from target values within specified pH tolerances.

#### **METHOD 1314: LIQUID-SOLID PARTITIONING AS A FUNCTION OF LIQUID-SOLID RATIO USING AN UP-FLOW PERCOLATION COLUMN PROCEDURE**

Method 1314 is an up-flow percolation column procedure used to evaluate the release of constituents from solid materials as a function of cumulative liquid-to-solid ratio (L/S). Method 1314 is equivalent to EN14405 and similar to CEN/TS 16637-3. Relative to field conditions, L/S can be a useful surrogate measure for time when infiltration rates are considered. In the context of the column test, L/S is defined as the volume of liquid passing through the column relative to the dry equivalent mass of test material in the column bed and is expressed in units of mL/g-dry. Approximately 300-600 grams of “as is” or air-dried solid material (moisture content less than ca. 20% dry basis) is packed under moderate compactive effort into a 5-cm diameter x 30-cm long column. The test material is packed in five “lifts” with each lift hand tamped using a 1-cm diameter rod. Layers of clean silica sand

are used at the top and bottom of the column to provide flow regulation on the inlet side and coarse filtration at the outlet. Leaching solution (eluent) is pumped upward through the material and eluate is collected as nine discrete volume fractions of the continuous elution volume. The up-flow percolation mode is intended to minimize air entrapment and flow channeling. The pump flow rate is adjusted to provide a volume of eluent equivalent to  $0.75 \pm 0.25$  L/S per day. For primarily inorganic materials, deionized water is used as the eluent for testing; however, a 1 mM solution of CaCl<sub>2</sub> may be used when testing certain materials (e.g., organic soils, clayey materials) where deflocculation of clay layers or dissolution of organic carbon may be a concern. The collection bottle is placed at a height of 6 to 12 inches above the column to provide sufficient hydraulic head to ensure flow while avoiding siphoning as well as to minimize backpressure which can cause leaks in the system. The nine eluate fractions are collected at specified L/S values of 0.2, 0.5, 1.0, 1.5, 2.0, 4.5, 5.0, 9.5, and 10 mL/g-dry. Analytical sample compositing is allowed depending on the intended use of the test results. The eluate pH, conductivity and (optionally) oxidation-reduction potential (ORP) are recorded for each fraction prior to filtration through a 0.45- $\mu$ m membrane and preservation of an analytical sample. After chemical analysis of analytical samples, cumulative release from the column at the specified L/S values is calculated from eluate concentrations and interval liquid-solid ratios (L/S<sub>i</sub>). The outputs of Method 1314 include the graphs of eluate concentration and cumulative release plotted as a function of L/S which are intended to illustrate changes in leaching that develop as percolation progresses and L/S increases.

**METHOD 1315: MASS TRANSFER RATES IN MONOLITHIC AND COMPACTED GRANULAR MATERIALS USING A SEMI-DYNAMIC TANK LEACHING PROCEDURE**

Method 1315 is a semi-dynamic tank leaching procedure used to determine the rate of mass transport from either monolithic materials (e.g., concrete materials, bricks, tiles) or compacted granular materials (e.g., soils, sediments, FA) as a function of time. Method 1315 is equivalent to EN 15863 and CEN/TS 16637-2. Monolithic test specimens may be cylinders or parallelepipeds, cast in molds or cut/cored to size from larger samples. Granular materials are compacted into cylindrical molds at optimum moisture content by Proctor-type compaction methods such as ASTM standards D698 (ASTM, 2007) or D1557 (ASTM, 2009). Monolithic specimens are unmolded and exposed to leachate on all faces while compacted granular specimens are exposed only on the axial face at the opening of the mold used to hold the compacted sample. Test specimens are leached in intervals in a series of tanks containing deionized water with each leaching interval having a specified duration. The volume of deionized water in each tank is based on the surface area of the test specimen at a liquid-to-surface area ratio (L/A) of 9 mL/cm<sup>2</sup>. At the end of each leaching interval, the test specimen is removed from the tank, the mass of the test specimen is recorded, and the specimen is submerged into another new tank containing fresh deionized water. The cumulative times corresponding to the end of the nine leaching

intervals are 2, 25, 48 hours, 7, 14, 28, 42, 49, and 63 days. For each tank eluate, the pH, conductivity, and (optionally) ORP are recorded prior to filtration through a 0.45- $\mu\text{m}$  membrane and preservation of an analytical sample. After chemical analysis, the mean flux of constituents in each interval (i.e., mass released per surface area per unit time of the leaching interval) and the cumulative release of constituents (total mass released per unit surface area as a function of time) are calculated from the eluate concentration, the volume of eluate collected for each interval, the geometry and mass of the test specimen, and the duration of each interval. In addition, mass transfer characteristics (e.g., diffusivity, tortuosity) may be calculated using assumed mathematical models. The outputs of Method 1315 typically used for environmental purposes include the interval mass flux ( $\text{mg}/\text{m}^2 \text{ s}$ ) and the cumulative mass release ( $\text{mg}/\text{m}^2$ ) as functions of cumulative time. This test is used to assess the combined effects of pore water chemistry (e.g., dissolution, adsorption) and diffusion through a monolithic or compacted granular material.

### **GEOCHEMICAL COMPOSITION**

Major, minor and trace element concentrations of leachates and solids from all types of tests will be analyzed using ICP-OES (Optima 5300, Perkin Elmer, USA) and ICP-MS (NexION™ 300D, Perkin Elmer, USA) instruments at the Geological Survey of Israel. Major and minor elements include Si, Al, Ca, Mg, Na, K, Fe, Ti, Mn, P, S, Ba, and Sr. Trace elements include the 20 elements which are regularly monitored for FA: Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V, Zn. Chloride ( $\text{Cl}^-$ ) concentration will be analyzed for leaching extracts using an ion chromatography system (ICS-2000, Dionex/Thermo, USA). In addition to the inorganic substances, total organic carbon (TOC) and total inorganic carbon (TIC) will be measured for the solid materials, and dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) will be measured for the leachates. All carbon analyses will be performed with a TOC analyzer (TOC-L, Shimadzu, Japan).

### **PHYSICAL AND MECHANICAL PROPERTIES**

Further tests will be conducted on the samples in order to characterize their physical, engineering and chemical composition throughout the whole process. These tests will include:

- Gradation (complementary analysis as some data exists at the NCAB).
- Laboratory Compaction Characteristics of Soil.
- Unconfined compression test.
- Water permeability test.
- Other tests that might be found necessary during the conduction of the research.

Gradation tests will be performed according to ASTM D6913 Standard Test Methods for Particle-Size Distribution (Gradation) of Soils Using Sieve Analysis.

The specimens for testing Laboratory Compaction Characteristics of Soil will be prepared according to ASTM D1557-12 - the ASTM Standard Test Method for Laboratory Compaction Characteristics of Soil Using Modified Effort (56,000 ft-lbf/ft<sup>3</sup> (2,700 kN-m/m<sup>3</sup>)). The modified effort test is sometimes referred in publications and specifications as the Modified Proctor Compaction Test (see also Section “Sample Preparation”). The relationship between molding water content and dry unit weight of soils (compaction curve) will be determined. The specimens will be compacted in a 4-in. (101.6-mm) diameter mold with a 10.00-lbf. (44.48-N) rammer dropped from a height of 18.00 in. (457.2 mm) producing a compactive effort of 56 000 ft-lbf/ft<sup>3</sup> (2700 kN-m/m<sup>3</sup>).

Unconfined compression test will be conducted according to ASTM D2166/D2166M - 16 – the ASTM Standard Test Method for Unconfined Compressive Strength of Cohesive Soil. This test method provides an important mechanical characteristic of the studied compacted granular materials (e.g., soils, sediments, FA) and is applicable only to cohesive materials, which will not expel or bleed water (water expelled from the soil due to deformation or compaction) during the loading portion of the test and which will retain intrinsic strength after removal of confining pressures.

Water permeability test will be conducted according to the ASTM D2434 - the ASTM Standard Test Method for Permeability of Granular Soils (Constant Head), or an equivalent method, which can be suitable for the studied materials.

Microstructural changes and changes in mineralogical composition of the materials after their aging and testing for unconfined compressive strength will be studied using Scanning Electron Microscope (SEM) and XRD (X-Ray Diffractometer), respectively.

## **DATA PROCESSING**

LeachXS – Orchestra will be used as the data management tool for data processing, storage and retrieval as needed in the project (Kosson et al., 2014b; Teutsch et al., 2017; Van der Sloot et al., 2008; van der Sloot et al., 2010).

The data generated by the testing according to the standard protocols described above will be loaded using LeachXS in the existing NCAB fly ash database (Teutsch et al., 2017). This allows cross comparison of leaching results and use of earlier data as basis for e.g. mixture modelling. Furthermore, the data once imported in LeachXS can be used for geochemical modelling to identify the release controlling phases in raw materials and in material mixes in relevant scenarios of FA application.

## MODELLING

The collective description of equilibrium reactions in multi-element, multi-phase systems is provided for individual CCPs by a chemical speciation fingerprint (CSF), which consists of a reduced set of aqueous-solid partitioning reactions, thermodynamic constants, and available contents (Kosson et al., 2014b). The CSF is derived primarily through evaluation of pH-dependence test data (EPA Method 1313 or analogous international methods) and literature information on relevant speciation, and verified as a function of liquid-solid ratio (L/S) by comparison to L/S-dependent test data (e.g., EPA Method 1314 or international analogues).

The input to the model consists of fixed element available contents (i.e., the amount of each element present that can participate in liquid-solid equilibrium partitioning) derived from the pH dependent leaching test results (maximum in the pH range 2-13), selected potential solubility controlling minerals (from thermodynamics databases in ORCHESTRA), active Fe- and Al-oxide sites, particulate organic matter (from humic acid and fulvic acid analyses) and a description of the DOC concentration as a function of pH (using polynomial curve fitting to pH dependent leaching test results). Although the organic matter content in fresh CCPs may be low, it may become a factor of relevance in the longer term in landfill disposal and ponds. The speciation of all elements is calculated in one problem definition within the model with a common parameter set and values. This substantially limits the degrees of freedom in selecting parameter values, because improvement of the model description for one element may deteriorate the outcome for other elements. Total carbonate is used as input parameter in the model (Branch et al., 2016).

### GEOCHEMICAL MODEL AND REACTION CONSTANTS

The CSFs for individual CCPs will be developed using the LeachXS/ORCHESTRA (LXO) software platform (ECN, 2012; Meeussen, 2003), which can lead to more generic virtual material descriptions to be used in subsequent reactive transport scenarios. LXO has the following embedded data sets of geochemical reactions:

- Liquid phase and mineral phase dissolution/precipitation reactions based on the MINTEQ V4 thermodynamic database file<sup>1</sup> and a collection of thermodynamic data from literature, such as the cement phases and solid solutions (e.g., C-S-H) based on the “cemdata2007” database (Lothenbach, 2014; Lothenbach et al., 2008) (Lothenbach et al., 2008).

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<sup>1</sup> The MINTEQ V4 database was translated from MINTEQA2 database described at <http://www2.epa.gov/exposureassessment-models/minteqa2>.

- Adsorption onto iron (hydr)oxide and aluminium oxide surfaces represented by the generalized two-layer model of (Dzombak and Morel, 1990) with or without modification for point of zero charge and site densities (Meima and Comans, 1998).
- Ion adsorption onto organic matter (i.e., fulvic acid and humic acid) and clay surfaces calculated with the NICA-Donnan model (Kinniburgh et al., 1999) including generic adsorption reactions as published by (Milne et al., 2001; Milne et al., 2003).

Through collection of individual literature data, additional reaction constants have been gathered in a separate thermodynamic database to extend the possible description of less common elements (e.g. As, B, Mo, Sb, Se, V). Additional reactions and reaction constants obtained from the literature or other databases (e.g., NEA Thermochemical Database Project,<sup>2</sup> Lawrence Livermore National Laboratory thermodynamic database that includes many inorganic constituents and radionuclides, etc.; Thermodem (Blanc et al., 2012), 2016) can easily be added or used in conjunction with LXO (Meeussen et al., 2009).

LeachXS/ORCHESTRA also has been verified and validated for leaching test data management and geochemical speciation based simulation of equilibrium simulations of generalized LSP, as well as for simulation of Method 1313, 1314 (in progress), 1315 and 1316.<sup>3</sup> The resulting specification of the virtual materials will be published so that they can be replicated on other geochemical speciation platforms (e.g., PHREEQC, Geochemist's Workbench) if desired.

The outcome of the speciation model provides virtual geochemical models of different FA types and blends with other materials (e.g., cement or soils) that can be used in reactive transport modelling of field scenarios for use of FA directly, blended with soils or cementitious materials with FA in infrastructure construction. Furthermore, the CSF will also be used to assess the effects of conditions outside the scope of actual laboratory testing conditions, such as a change in redox state, ingress of DOC (dissolved organic carbon), and carbonation by CO<sub>2</sub> uptake from the atmosphere. Field data, literature and local information will be collected to provide information on the relevant range of conditions to be chosen for sensitivity analysis to be performed in assessing impact from selected ash utilisation scenarios.

## **MIXTURE MODELING**

In LeachXS, a tool has been developed that allows modelling of material mixtures starting from the CSFs of individual components constituting the mix. This modelling concept allows an identification of the transition of solubility control by one matrix control by one

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<sup>2</sup> Information of the NEA Thermodynamic Database is available at <https://www.oecd-nea.org/dbtdb/>.

<sup>3</sup> LeachXS/Orchestra has undergone software verification and validation (V&V) consistent with nuclear quality assurance (NQA-1 graded approach) to support field performance assessment of leaching for nuclear waste management applications. V&V has been completed for laboratory simulations of generalized LSP and Methods 1313, 1315 and 1316, with Method 1314 verification and validation currently in progress (anticipated completion by the end of 2017).

matrix to the other in the mix. Grout and controlled low strength materials are a blend of FA with cement, FA in embankment consists of FAs from different origin and some infrastructure applications will consist of mixtures of FA with soils. Therefore, a mixture corresponding with the estimated proportions of the individual components (e.g., FA, cement, soils) contributing to the material as used in selected scenarios will be modelled in a stepwise mode starting from pure FA (main contribution). A key aspect will be to what FA mixture ratios will the controlling leaching chemistry shift from that of FA to that of the added components (e.g., cement or soil). Earlier work has demonstrated that cement chemistry is controlling for many cement-FA mixtures up to 40% substitution of FA for cement (Garrabrants et al., 2014; Kosson et al., 2014a; van der Sloot et al., 2012).

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