Pre-proposal for a Joint Research Program

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

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12 June 2013

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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[1]. 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. 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. 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. In the various applications in which FAs are utilized, the FA comes in contact with other substances which could influence its characteristics, such as cement in concrete mix or soils and other materials in agricultural application and infrastructure construction. 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 or blended with soil as part of a soil supplement, the leaching characteristics of the resultant material could be different than the component materials. Consequently, the basic approach of this research proposal is to understand the FA mixtures as a whole by studying the raw materials, 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.

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., 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 (EPA, 2012a; EPA, 2012b). Analogous test methods are also being finalized in Europe through the European Committee for Standardization (CEN) for use in evaluation of waste, soil, sludge and construction products. 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. The leaching tests include:

- **Method 1313**: Liquid-Solid Partitioning (LSP) as a Function of Eluate pH Using a Parallel Batch Extraction Procedure

[1] 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.

- **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 outputing 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 (EPA, 2009) and FA derived products (EPA, 2012c) 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. EPA's current efforts provide a unique opportunity for synergistic collaboration with Israeli researchers and regulators for development of an analogous environmental assessment and criterion development framework that is tailored to Israel's unique geography and needs.

The overall research goal is to provide a risk-informed environmental safety assessment framework based on LEAF for evaluation of beneficial use of coal fly ash that is tailored to Israeli needs. The resulting data and methodologies then can be used by regulators to establish specific FA use criteria. The results of this research program also can serve as a pilot program for broader use of the LEAF framework for risk informed decision making regarding beneficial use, disposal and remediation of a range of materials. The specific research objectives are:

1. (i) increase familiarity and efficiency in use of EPA Leaching Environmental Assessment Framework (LEAF) test methods and interpretation approaches, along with use of LeachXS as a data management and evaluation tool.

   (ii) develop a LeachXS database of all results from testing of Israeli coal ash samples and ash derived products, along with comparative information from other sources.

2. evaluate the effect of high FA use rates in concrete and cementitious materials to understand the upper bounds to potential usage rates[2].

3. evaluate the potential for agricultural use of FA (and FA-containing products) based on testing results from Israeli reference soils and ashes.

4. develop and recommend a framework, with example calculations, for evaluation of FA use in paving, infrastructure and agricultural applications that would be tailored to specific Israeli conditions.

The proposed research is based on a national and international collaboration of a team with relevant experience and expertise in the proposed field of study. The research program will be overseen by a Scientific Advisory Committee comprised of representatives from NCAB, Israeli regulatory authorities and EPA.

The cost estimate included in this proposal takes into consideration extensive leveraging of resources and activities currently being supported by other mechanisms. For example, current work on behalf of EPA and the EU substantially reduces the costs associated with participation by Vanderbilt University and Hans van der Sloot Consultancy. In addition, personnel costs included in the budget for Israeli organizations are substantially reduced because of salaries paid through the home institution (e.g., GSI, Technion, Volcani) by the Israeli government.

SCIENTIFIC ADVISORY COMMITTEE FOR THE RESEARCH PROGRAM

This large scale proposal combining participants from Israel and abroad is aimed at providing further basis for better understanding Israeli FA properties and optimizing its implementation in various applications. As these applications introduce the FA to a variety of environmental compartments, we seek to involve the Israeli authority bodies responsible for the environment and public health. In this way, we believe the needs and demands of the regulatory bodies will receive full coverage. In the end, this research must address the needs of the regulators and industry to achieve a consensus-based path forward for FA use. Therefore, we suggest creating a Scientific Advisory committee for the research program which will engage in the planning and follow the research team in all stages to completion.

The specific tasks and responsibilities of the committee will be:

(1) to insure that critical questions regarding coal ash use in Israel are being addressed;

(2) to review specific experimental objectives and plans;

[2] We recognize that properties of the FA other than leaching chemistry may further limit usage rates in certain applications, for example, radionuclide content may restrict usage rates in certain concrete uses more than leaching.

(3) to review results and reports prior to finalization;

(4) to provide the research team with input on Israeli and US and perspectives on coal ash use, including related initiatives within their respective organizations; and,

(5) to insure that research will provide needed support to development of practical and relevant Israeli regulations.

The Scientific Advisory Committee also should provide comments on this preproposal so that their input can be addressed in the final proposal.

We suggest the following bodies to participate in the Scientific Advisory committee:

1. The Israel Ministry of Environmental Protection,
2. The Israel Ministry of Health,
3. Israel Water Authority,
4. Israel Ministry of Agriculture,
5. National Coal Ash Board (NCAB), and
6. US Environmental Protection Agency (EPA) both from scientific and regulation perspectives.

The Scientific Advisory Committee for the research program should meet both electronically and in-person as appropriate. Electronic meetings should take place at least quarterly and in-person meetings at least annually.

We recommend that one meeting of the Scientific Advisory Committee occurs at the US EPA with a coordinated visit to Vanderbilt University. This will allow for broader exchanges between the Israeli Scientific Advisory Committee members, researchers and EPA and VU participants. In addition, this will allow for direct observation and discussion about the implementation of the LEAF test methods and evaluation framework in the United States.

TASK 1 – ENHANCING ISRAELI CAPABILITY IN USE OF LEAF AND LeachXS

PARTICIPANTS

Nadya Teutsch, David S. Kosson and Hans van der Sloot

OBJECTIVES

1a. Increase Israeli familiarity and efficiency in use of EPA Leaching Environmental Assessment Framework (LEAF) test methods and interpretation approaches, along with use of LeachXS as a data management and evaluation tool.

1b. Develop a LeachXS database of all results from testing of Israeli coal ash samples by GSI and NCAB from 2007 to present and ash derived products (i.e., cement materials testing), along with comparative

information from other sources. Provide an initial set of comparisons and base statistics for use with the NCAB/GSI data sets.

1c. Develop and assist with initial set up of a quality control framework for monitoring FA leaching characteristics using LeachXS.

APPROACH

1a. Initial training on LeachXS use for data management has been provided to GSI and NCAB by D. Kosson. Additional training will be provided by D. Kosson via web-meetings (such as using GoToMeeting or similar internet tools) as needed on LEAF test methods implementation and LeachXS use for data management and analysis. NCAB will purchase for the GSI one license of LeachXS Pro (for use on two computers) and will be provided additional free LeachXS Lite licenses as needed. Additional training and free LeachXS Lite licenses (or paid LeachXS Pro licenses) may be provided to personnel of Israeli ministries (e.g., Environment, Health, Water Board) but are not included in this proposal.

1b. NCAB and GSI will input Israeli leaching data into LeachXS templates (already partially completed) and VU will assemble an initial database with Israeli, US EPA and other international data (provided by HvdS). D. Kosson and H. van der Sloot will work with GSI and NCAB to develop the initial set of comparisons and a summary report providing documentation of the database and comparisons. GSI along with NCAB will then be responsible for maintaining the resulting database through input of new data as developed and providing data comparisons as needed.

1c. D. Kosson and H. van der Sloot will work with GSI and NCAB to implement applicable quality control tools in LeachXS Pro as needed for on-going monitoring of leaching characteristics and total elemental content of Israeli produced coal combustion residues. Example output and a guidance document on use of the system will be provided.

ANTICIPATED PRODUCTS

1a. One LeachXS Pro license for use on two computers, unlimited number of licenses of LeachXS Lite, training of GSI and NCAB personnel on use of LeachXS Pro and LeachXS Lite for data management, training of GSI personnel on efficient implementation of LEAF test methods.

1b. LeachXS database with Israeli coal ash data, US EPA data and international data on coal combustion residues and derived products (i.e., cement materials, etc.); Summary report containing documenting contents of the provided database and example comparisons.

1c. A quality control framework for Israeli coal combustion residues that assists with regulatory compliance implemented in LeachXS Pro, including initial training and documentation for GSI and NCAB.

SCHEDULE AND MILESTONES

1a. This task has been initiated and will continue on as needed. Trial licenses of LeachXS Pro have been provided to GSI and NCAB and will be extended through August 2013.

1b. *Authorization is sought to proceed immediately with completion of Tasks 1a and 1b*. This will facilitate retention of knowledge gained through initial training. Input of existing Israeli data into Excel templates should be completed prior to the end of August 2013. The resulting database and initial comparisons will be developed during until October 2013, with a draft summary report provided for review in November 2013.

1c. This task can proceed at any time after completion of Task 1a and 1b and will take 3 months to complete.

TASK 2 – DEFINING PHYSICAL-CHEMICAL LIMITS IN USE OF FLY ASH IN CONCRETE AND CEMENTITIOUS MATERIALS

PARTICIPANTS

Nadya Teutsch, David S. Kosson, Hans van der Sloot, Andrew Garrabrants and Konstantin Kovler

OBJECTIVES

2a. Evaluate the current data set and earlier GSI research samples of grout and controlled low-strength material (CLSM) for the impact of partial carbonation during curing, because related studies have indicated the potential for carbonation to increase leaching of some constituents of potential concern (i.e., arsenic).

2b. Evaluate the effect of high FA use rates in concrete and cementitious materials to understand the transition point in usage rates of FA when leaching chemistry is controlled by cement chemistry to when leaching chemistry is controlled by FA chemistry. This will provide the "tipping point" and basis for defining an upper bound to FA usage rates.

APPROACH

2a. The monolith data produced by GSI on grout and CLSM will be evaluated in the context of related testing at VU and in The Netherlands. Selected monoliths remaining at GSI will be evaluated for the depth of carbonation and leaching by GSI. Method 1313 will be completed by GSI on the earlier produced grout and CLSM samples. 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 and new Method 1313 results.

2b. **(i)** Preparation of a quality assurance project plan (QAPP) with review by EPA quality assurance personnel and the Scientific Advisory Committee. **(ii)** Chemical speciation modeling of cement:FA mixing ratios and consequences for leaching for a representative Israeli FA and EPA FA; this will serve as the basis for designing experimental test cases. **(iii)** Formulation and preparation of 2 mixes with a representative Israeli FA (by GSI and Technion) and 2 mixes with EPA FA (by VU), followed by 6 months curing and then testing using Methods 1313 (pH dependence) and 1315 (monolith).

ANTICIPATED PRODUCTS

2a. A manuscript for a peer-reviewed journal that documents results of grout and CLSM testing and modeling.

2b. A QAPP for review by EPA and the Scientific Advisory Committee; briefing to the Scientific Advisory Committee on the results of initial system modeling; a manuscript for a peer-reviewed journal that documents the results of modeling and testing to define the physical-chemical limits of FA usage in cementitious materials; all new data will be added to NCAB/GSI LeachXS database; briefing to the Scientific Advisory Committee on results of Tasks 2a and 2b.

SCHEDULE AND MILESTONES

2a. This task will take 8 months to complete from approval to proceed (FATP).

2b. Draft QAPP -1 month FATP; Initial modeling 2 months FATP; materials preparation – 4 months FATP; initial leaching testing – 10 months FATP; completion of leaching testing - 14 months FATP; draft manuscript – 18 months FATP.

TASK 3 – TESTING AND MODELING IN SUPPORT OF EVALUATING AGRICULTURAL USE OF FLY ASH

PARTICIPANTS

Nadya Teutsch, David S. Kosson, Hans van der Sloot, Pinchas Fine and Avner Silber

OBJECTIVES

3a. Evaluate leaching behavior of FA-sludge mixtures and FA-sludge mixtures applied to Israeli agricultural soils.

3b. Evaluate plant uptake of constituents of potential concern from FA-sludge mixtures applied to Israeli agricultural soils.

APPROACH

3a. **(i)** Develop QAPP for EPA and Scientific Advisory Committee review (GSI and Volcani). **(ii)** Method 1313 testing for 2 Israeli reference soils,1 sludge sample and 1 FA/sludge product (by GSI); Method 1314 (percolation column) testing of 2 Israeli reference soils (by GSI). **(iii)** Chemical speciation pH dependence leaching modeling of FA, sludge, FA/sludge mixture (product), and product application to reference soils; chemical speciation percolation scenario modeling of FA application to reference soils (by H. van der Sloot and D. Kosson). **(iv)** Method 1313 for sludge/FA mixtures (2 ratios), and sludge/FA/soil mixtures (2 loading rates, 1 FA/sludge ratio, 2 soils; 6 cases total, by GSI); Method 1314 for sludge/FA/soil mixtures (2 loading rates, 2 soils; 4 cases total by GSI); Method 1314 columns with blended sludge/FA/Soil followed by soil only columns, (1 application rate, 2 soils; 2 cases total, this task is optional and only to be completed if significant leaching is indicated from the Method 1314 testing in the prior step). **(v)** Chemical speciation modeling (pH dependence and percolation column scenarios) to compare experimental results with modeling results and quantify simulation uncertainties.

3b. **(i)** Review of past/current studies and results with research team and Scientific Advisory Committee. **(ii)** Develop QAPP for EPA and Scientific Advisory Committee review (GSI and Volcani) **(iii)** Experimental program to be defined after review of past/current studies and results with the research team and Scientific Advisory Committee **(iv)** Compare release and chemical form of release as defined by leaching tests/modeling with uptake by agricultural products taking into account distinction between product (e.g., fruit, grain, etc.) and non-product foliage (Volcani, GSI, VU, H. van der Sloot).

ANTICIPATED PRODUCTS

3a. QAPP for EPA and Scientific Advisory Committee review; new test data added to NCAB/GSI LeachXS database; manuscript for peer-reviewed journal; briefings on results for Scientific Advisory Committee.

3b. QAPP for EPA and Scientific Advisory Committee review; manuscript for peer-reviewed journal; briefings on results for Scientific Advisory Committee.

SCHEDULE AND MILESTONES

3a. Draft QAPP – 3 months FATP; Method 1313 results for (ii) – 6 months FATP; Modeling results for (iii) – 8 months FATP; Method 1313 and 1314 results – 12 months FATP; Modeling results for (v) – 16 months FATP; draft manuscript detailing results – 20 months FATP.

TASK 4 – DEVELOPING A FRAMEWORK FOR RISK INFORMED DECISIONS FOR ISRAELI BENEFICIAL USE OF FLY ASH

PARTICIPANTS

Nadya Teutsch, David S. Kosson, Andrew Garrabrants, Hans van der Sloot, Pinchas Fine (agricultural applications), Avner Silber (agricultural applications) and Konstantin Kovler (construction applications)

OBJECTIVES

4a. Provide an overarching framework for risk-informed decision making for beneficial use of FA that also can be used to evaluate beneficial use and disposal of other secondary materials and wastes.

4b. Develop a set of scenario definitions to serve as the evaluation basis for each potential use of FA. Potential FA use applications to be included in the evaluation are

- Use of FA in cementitious materials, such as grouts, mortars, CLSM and concrete structures
- Use geotechnical applications (soil stabilization, grouting, etc.)
- Road base application
- Roadway fill and embankment
- Agricultural use for soil improvement and fertilizer

4c. Define a set of geographic regions within Israel for LEAF evaluations and develop a dataset of relevant parameters for each region from existing climate, geologic, hydrologic and agricultural data.

4d. Define the calculation basis and provide example calculations for potential FA use and prototype examples.

APPROACH

4a. VU in collaboration with all other partners will draft a report that provides the overarching framework as to be tailored for Israeli conditions and considering the identified use applications.

4b. VU, GSI and HvdS, in collaboration with other partners as appropriate (i.e., Technion for construction applications, Volcani for agricultural applications) and with input from the Scientific Advisory Committee will establish a set of application specific scenario definitions for each potential FA use.

4c. GSI with input from the other partners and the Scientific Advisory Committee will delineate geographic regions within Israel for regional evaluations and necessary geographic data needed for each region. GSI will then assemble and provide the needed data sets in electronic form (e.g., Excel spreadsheets) along with a summary report that documents the data sets.

4d. VU, HvdS and GSI, in collaboration with other partners as appropriate (i.e., Technion for construction applications, Volcani for agricultural applications), will define and document the evaluation

basis and calculations needed to provide the leaching source term and subsequent use of the derived source term for each potential FA use. Example calculations will be provided.

ANTICIPATED PRODUCTS

4a. A report providing a high level description of the approach for using LEAF in FA use decisions tailored to Israeli conditions.

4b. A report or series of reports[3] providing applicable scenario definitions for each potential FA use.

4c. A report delineating appropriate geographic regions and documenting data sets, along with electronic files with the applicable data sets for each region.

4d. A report or series of reports[2] documenting the evaluation basis and calculations needed for each potential FA use.

SCHEDULE AND MILESTONES

4a. Draft report 2 months after initiation of Task.

4b. Definition and draft documentation of each scenario will require 1.5 months (if separate reports are desired) or 6 months (if one report is desired) and will be initiated after completion of Task 4a. The detailed schedule will be based on priorities to be established with input from the Scientific Advisory Committee and available funding.

4c. Completion of this task will require 4-6 months and can be initiated after completion of Task 4a and carried out in parallel with Task 4b.

4d. Definition and draft documentation of each scenario will require 2 months (if separate reports are desired) or 8 months (if one report is desired) and will be initiated after completion of Task 4b. The detailed schedule will be based on priorities to be established with input from the Scientific Advisory Committee and available funding.

It is also anticipated that several manuscripts for publication in peer-reviewed journals will result from integration of the results from Task 4.

[3] Whether a single encompassing report, or a series of reports with each report specific to a single potential FA use are developed will depend on the priorities, schedule and funding availability agreed on with the NCAB after input from the Scientific Advisory Committee.

GENERAL TERMS AND CONDITIONS

The following general terms and conditions will apply to this research program:

1. All communications and reports made as part of this project will be in English.
2. EPA participation in this research program will be consistent with the Memorandum of Understanding between EPA and the Israeli Ministry of Environment.
3. All travel by researchers for project meetings will be reimbursed directly by the NCAB and will require prior approval by NCAB to be reimbursable.
4. Travel by the Scientific Advisory Committee members will be paid either by the NCAB or the committee member's host institution based on prior arrangements agreed upon by NCAB and the committee member's host institution.
5. Licenses for general work purposes (e.g., Word, Excel, etc.) and communications (Gotomeeting, e-mail, etc.) will be the responsibility and cost of each participant.

REFERENCES

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EPA (2012b). Interlaboratory Validation of the Leaching Environmental Assessment Framework (LEAF) Method 1314 and Method 1315. EPA 600/R-12/624.

EPA (2012c). The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material on the Leaching of Constituents from Cements and Concretes. EPA 600/R-12/704.

Kosson, D. S., H. A. v. d. Sloot, F. Sanchez, and A. C. Garrabrants (2002). An Integrated Framework for Evaluating Leaching in Waste management and Utilization of Secondary Materials. Environmental Engineering Science, 19(3): 159-204.

LEAF http://www.vanderbilt.edu/leaching/