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Robert Moser, MD, Secretary

Department of Health & Environment

Sam Brownback, Governor

July 16, 2013

William C. Anderson
Doerner, Saunders, Daniel & Anderson, L.L.P.
Two West Second Street, Suite 700
Tulsa, Oklahoma 74103-3117

RE: Removal Site Evaluation Work Plan for Phase 1 Testing: *In Vitro* Bioaccessibility Study for Metals in Soil at Cherryvale, Kansas
Former National Zinc Site, Cherryvale, Kansas
KDHE Project Code #C3-063-00026; Consent Order Case #03-E-0022

Dear Mr. Anderson:

The Kansas Department of Health and Environment (KDHE) acknowledges receipt of the above-referenced document, submitted and prepared by Exponent on behalf of the United States Steel Corporation (U.S. Steel Corp.) and Citigroup Global Market Holdings, Inc. (Citigroup), dated May 2013, and received June 4, 2013. KDHE has completed its review and approves the document with the following comments.

1. Scope of Work: The Work Plan indicates the information obtained from the Bioaccessibility Study will be incorporated into the calculations presented in KDHE's Risk-Based Standards for Kansas (RSK) Manual. KDHE's current Tier 2 residential scenario soil pathway for lead is 400 milligrams per kilogram (mg/kg), and 18.9 mg/kg for arsenic. For the record, although not explicitly stated in the RSK Manual, the arsenic value is based on a default relative bioavailability (RBA) value of 60%, and the lead value is established based on the Integrated Exposure Uptake Biokinetic (IEUBK) Model for Lead in Children using default input parameters. No revision to the Work Plan is required.

2. Sample Locations: As discussed previously during a June 14, 2013 teleconference between KDHE and Respondents regarding sample locations, page 3 of the Work Plan indicates that one composite sample will be collected from Logan Park from the areas around the track with apparent smelter fill material visible at the surface; however, Figure 1 in the Work Plan shows two sample locations for Logan Park, one being near the ticket booth southeast of the track, and one north of the track near the high jump pit area. For the record, KDHE requested on June 14, 2013 that two composite samples be collected from Logan Park as indicated in Figure 1, and Respondents agreed with KDHE's request. No revision to the Work Plan is required.

3. Sample Locations: The last paragraph of Page 3 of the Work Plan states "*The effort will also include samples from the area of the city ball fields, notwithstanding general agreement between KDHE and Respondents that the ratio of different metals in samples collected from this area, together with information about land use, suggests that the elevated levels of arsenic in this area are the result of historical use of arsenical pesticides, rather than originating from distributed smelter waste*". KDHE agrees that the relative concentrations of arsenic and lead near the city ball fields differ from other areas in Cherryvale and may be related to historical pesticide use. KDHE anticipates that the Phase 1 and Phase 2 testing in this area will help resolve this issue.

4. Extraction Testing: The Work Plan indicates that to ensure good data quality, extraction efforts will include a matrix spike, a blank, a standard reference material (SRM), and a triplicate extraction of one soil, at a frequency of at least once per every 20 site soil samples. For clarification purposes, based on discussions with Yvette Lowney of Exponent on July 11, 2013, KDHE understands that a reagent blank, bottle blank, blank spike, matrix spike, duplicate sample (triplicate analysis of one sample), and a SRM control sample will be collected for quality control purposes. No revision to the Work Plan is required.

William C. Anderson,
Doerner, Saunders, Daniel & Anderson, L.L.P.
July 16, 2013
Page 2 of 2

5. Exhibit A - Soil Sampling Procedure: Page 3 of Exhibit A (Sample Locations) proposes that soil samples will be collected at a depth from 0 to 2 centimeters (cm) from the soil surface. If grass is present, the grass layer will be peeled back with hand tools to expose the underlying soil immediately below the grass root zone and the 2 cm sample will be collected from this layer. As removing the grass layer and then collecting the 2 cm sample below the grass layer will likely remove the uppermost soil, KDHE recommends incorporating any adhered soil to the grass layer into the soil sample for analysis. Based on discussions with Yvette Lowney of Exponent on July 9, 2013, KDHE understands that the requested change in procedure will be implemented and followed in the upcoming sampling activities. No revision to the Work Plan is required.

No written response to this letter is required by KDHE. KDHE appreciates Respondents diligence in working with KDHE to address matters within the Cherryvale community, and looks forward to implementing Phase 1 RSE field activities this summer. Should you have any questions regarding this letter, please contact me by phone at 785-296-6242 or email at hburke@kdheks.gov.

Sincerely,

Holly Burke

Holly Burke
Environmental Scientist
Remedial Section/Site Restoration Unit
Bureau of Environmental Remediation

c: Chris Carey, KDHE →Former National Zinc Site File – C3-063-00026
Nancy Ulrich, KDHE Office of Legal Services
Andrew Thiros, U.S. Steel Corp.
Mark Rupnow, U.S. Steel Corp.
John Preston Turner, Citigroup
Mark Landress, Project Navigator, Ltd.
Travis Kline, TechLaw, Inc.
Yvette Lowney, Exponent

FINAL

APPROVED WITH COMMENTS
DATE(S) 7/16/2013, H.R.

Removal Site Evaluation Work Plan for Phase I Testing: *In Vitro* Bioaccessibility Study for Metals in Soil at Cherryvale, Kansas

Exponent scientists have reviewed data regarding arsenic, cadmium, lead, and zinc (hereafter referred to as “metals,” although arsenic is technically classified as a metalloid) in soils in the area surrounding the former National Zinc Smelter site in Cherryvale, Kansas (the Site). Available information and analytical reports indicate that historical smelter emissions may have impacted areas of town near the location of the former facility, smelter waste may have been deposited in various areas around town, and some soils demonstrate elevated levels of some metals. Additionally, different areas of town show different “signatures” of metals in soil, where the ratios of the elements vary at different locations.

This Removal Site Evaluation (RSE) Work Plan — Phase 1 documents a scope of work that would allow for characterization of soils from areas of town, specifically focused on generating data to understand the relative oral bioavailability (RBA) of metals from these soils. Once defined, these RBA values can be used to increase the accuracy of health-based screening values for application in Cherryvale by incorporating this site-specific information. Based on the results of this RBA testing, an RSE Work Plan — Phase 2 will be developed that will describe sampling and analysis to delineate the nature and extent of soils that exceed the site-specific risk-based screening levels.

Based on analytical results for the site,^{1,2} lead and, to a lesser extent, arsenic are the metals of primary interest. This determination is based on a screening of site data against risk-based standards for Kansas.³ The existing database regarding arsenic and lead indicates that soil characteristics and the source of chemicals to the soil can exert controls on the RBA of metals from soil, and that the RBA varies on a site-specific basis. For many soils, the relative oral bioavailability of these metals is significantly lower than default values proposed by regulatory agencies. This has been particularly well established for metals in soils that have been affected by mining- or smelting-related activities. However, meaningful adjustments are difficult to achieve without site-specific data. For this reason, this Work Plan outlines the development of site-specific bioavailability adjustment values for lead and arsenic in soils at the Site. This document outlines the conceptual components that will be incorporated into the testing. The

¹ “Analytical Results from KDHE” as reported at the Cherryvale Kansas Residential Site Inspection Meeting, December 3, 2012. Prepared by Project Navigator, Ltd., for KDHE Bureau of Environmental Remediation, on behalf of Citigroup Global Market Holdings, Inc., and U.S. Steel Corporation.

² Phase III Brownfields Assessment. March 26, 2012. Prepared by Terracon Consultants, Inc., for City of Cherryvale, KS. Terracon Project No 14107010.

³ Kansas Department of Health and Environment. Bureau of Environmental Remediation. RSK Manual – 5th Version. October 2010.

attached Sampling Procedure (Exhibit A, attached) defines specific technical aspects of the associated sampling effort.

Under this effort, Exponent has worked with U.S. Steel Corporation and Citigroup Global Market Holdings, Inc. (Respondents) and their consultants to identify locations for samples for *in vitro* bioaccessibility and mineralogical analysis, and will coordinate with laboratories for analyses, compile results, interpret the results in the context of soils that have been well characterized with regard to lead or arsenic bioavailability, and present the results and findings in a report for review by the Kansas Department of Health and Environment (KDHE). Details are provided below and in the attached Standard Operating Procedure (SOP). The deliverable for this task will be a brief report on the methods and results of the evaluation. This information will be used to support site-specific bioavailability adjustments to the Risk-Based Standards for Kansas, provided by KDHE.

Specific Scope of Work for *In Vitro* Bioaccessibility Study

Exponent proposes to estimate the relative oral bioavailability of arsenic and lead in 18–21 soil samples from the area. The sample locations were selected in a manner that biases the study materials to specifically include soils that appear to be in direct contact with smelter waste that may have possibly originated from the Site, as well as possible aerial deposition from the Site.

Sample Locations

These samples will be collected from various areas around the site to characterize potentially different sources of metals to the soil, and to assess the relative oral bioavailability of the metals from soils across the Site. The specific sampling locations were determined based on discussions among Exponent, Respondents, and KDHE and their consultants, and include samples from locations in the neighborhood abutting the former smelter site, as well as locations farther from the former smelter site. All samples will be collected from the top two cm of the soil surface (as further described in Exhibit A). Locations are based on areas that appear to have elevated levels of lead and arsenic in soil, as defined by existing data, and areas where visual inspection indicates the possible presence of smelter waste materials. The sample locations were selected in a manner that biases the study materials, to the extent possible, to specifically include soils that are in direct contact with possible smelter waste, as well as possible aerial deposition from the Site.

The specific samples targeted for the evaluation, and the rationale for selecting each sample, are described below. The attached map (Figure 1 to Exhibit A) provides an indication of the approximate locations for each sample.

- **Ditches:** Three samples, each a composite of surface soil from ditches around town with what appears to be visible crushed smelter retorts and/or slag, one of which would be from the ditches across the street from Cherryvale Middle School (“CSM Ditch 1-4” on the KDHE map).

- Adjacent to sidewalks where smelter waste material appears to have been used as underlayment: Three composite samples of surface soils adjacent to sidewalks, one from near Thayer school, and two from other areas of Cherryvale where it appears that the smelter waste material underlayment is visible at the surface.
- Ballfield: Two surface soil composites from the area where it appears that visible granular smelter slag is present.
- Residential area impacted by historical aerial deposition from the smelter: Four composite surface soil samples from residences near EPA's residential removal action area. Samples will be generated from a three-point composite from areas of the residential yard that are away from the drip line of the house, and specifically not target areas impacted by what might appear to be smelter waste. These yard composites will be generated from six distinct residences (subject to access agreement), screened in the field for lead concentration by XRF, and the four composite samples with the highest lead concentrations of the six residences will be selected for bioaccessibility testing.
- Residential area(s) with apparent smelter slag/waste material: Five to eight composite surface soil samples to capture the different types of materials deposited in residential areas of Cherryvale. The composite from residential yards will be composed of surface soil samples of at least three subsamples from the area affected by apparent smelter waste, and away from the drip line of any structure. Any visual characteristics of the apparent smelter waste material will be recorded, to see if they correlate with analytical results, once received.
- Logan Park: one composite sample from the areas around the track with apparent smelter fill material visible at the surface.

The attached map (Figure 1 to Exhibit A) provides an indication of the location from which each sample will be collected. For residential areas, probable sample locations have been identified. The specific properties will be identified in the field, based on visual inspection, access agreements, and identification of the apparent presence of smelter waste material, prior to sample collection.

Consistent with recommendations from KDHE and their consultant, each sample will be a composite from three to five discrete locations. The composites will be generated in a manner to allow characterization of specific geographic areas within Cherryvale (e.g., residential areas near the prior EPA residential removal action, where yards may be impacted by historical smelter emissions, or for ditches around the city), or to characterize the RBA of metals from soil associated with what appears to be specific smelter waste materials (e.g., different types of slag). The effort will also include samples from the area of the city ball fields, notwithstanding general agreement between KDHE and Respondents that the ratio of different metals in samples collected from this area, together with information about land use, suggests that the elevated

levels of arsenic in this area are the result of historical use of arsenical pesticides, rather than originating from distributed smelter waste.

Prior to bioaccessibility testing or any other sample characterization, Respondents will provide to KDHE a map indicating the final sample locations, including any changes to initial plans that may have emerged during sample collection (e.g., lack of material or access issues). In other words, before analytical work is initiated, the sample location map (Figure 1 of Exhibit A) will be updated to reflect any modification of sample locations, and will be provided to KDHE.

Extraction Testing

All of the soil samples will be tested for bioaccessibility using a physiologically based extraction test to establish the fraction of metals that could be liberated in the gastrointestinal tract and would be available for absorption. In this effort, the RBA of lead will be estimated in accordance with existing EPA guidance and Standard Operating Procedures for the use of *in vitro* data for determining RBA of lead in soils (included as Exhibit B). For arsenic, the RBA will be based on a weight-of-evidence approach that includes *in vitro* bioaccessibility testing of the soils using the EPA method for lead, together with information on the mineralogy of the metals in soils. These results will be interpreted in the context of other soil samples for which the RBA of arsenic has been investigated in animal studies.

Based on sample provenance and the results of the *in vitro* testing, a subset of the soil samples (five assumed) will be evaluated for mineralogy, to establish the specific forms of the metals present. The bioaccessibility extractions and the mineralogy evaluation will be performed on the <250- μ m particle size fraction collected by sieving bulk soils, to provide information on the fraction of soil that is believed to contribute to oral exposures. Samples may need to be disaggregated, but will not be ground. Mineralogy will be analyzed using electron microprobe techniques, according to the methods specified in the SOP attached as Exhibit C.

The laboratory work, including sample preparation, *in vitro* extraction to determine bioaccessibility, and analysis of sample mineralogy, will be performed by Dr. John Drexler at the Laboratory for Environmental and Geochemical Studies (LEGS) at the University of Colorado at Boulder, and coordinated by Exponent staff. This laboratory was selected for the bioaccessibility testing because of Dr. Drexler's long-term involvement with the development and application of *in vitro* test methods for assessing the RBA of metals from soil. His research (Drexler and Brattin 2007) forms the technical basis for EPA's guidance regarding the use of *in vitro* methods for estimating the RBA of lead in soils.

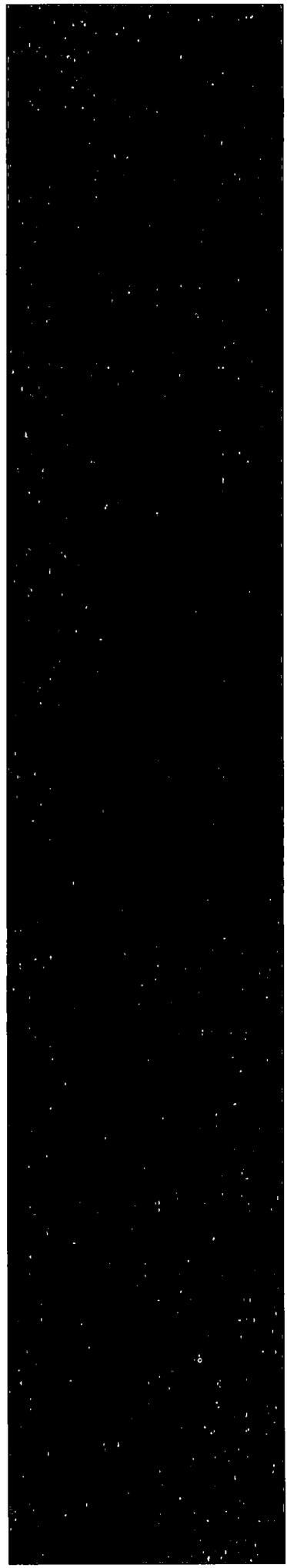
To ensure good data quality, extraction efforts will include a matrix spike, a blank, a standard reference material (SRM), and a triplicate extraction of one soil, at a frequency of at least once per every 20 site soil samples. Bioaccessibility and mineralogy data will be compiled and interpreted by Exponent with regard to the likely bioavailability observed at the Site.

Findings will be reported in a technical memorandum presenting the test methods, analytical results, and an interpretation of the mineralogy and extraction results in terms of assessing the oral bioavailability of arsenic and lead from the test soils.

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Prepared at Request of Counsel

Exhibit A

Soil Sampling Procedure for Soil Bioaccessibility Testing





Memo

To: Yvette Lowney, Walt Shields (Exponent)
From: Mark Landress, P.G.
Date: May 31, 2013
Project No.: 04-119.400
Re: National Zinc Cherryvale Bioaccessibility Sampling Plan

Yvette,

Please find attached the final version of the bioavailability sampling plan prepared by Project Navigator, Ltd., which we understand will be included as Appendix A to Removal Site Evaluation Work Plan for Phase I Testing, In Vitro Bioaccessibility Study for Metals in Soil at Cherryvale, Kansas.

If you have any questions please give me a call in my office at 713-468-5886 or on my cell at 713-539-3636.

Regards,

Mark Landress

Cherryvale, Kansas Soil Bioaccessibility Sampling Procedure

Prepared for:
Kansas Department of Health and Environment

Prepared by:
Project Navigator, Ltd.
10497 Town & Country Way Suite 830
Houston, TX 77024

On behalf of:
United States Steel Corporation and
Citigroup Global Market Holdings, Inc.

May 2013

Cherryvale, Kansas Soil Bioaccessibility Sampling Procedure

This Soil Bioaccessibility Sampling Procedure has been prepared to support data collection for soil characterization for Removal Site Evaluation Work Plan for Phase I Testing: *In Vitro* Bioaccessibility Study for Metals in Soil at Cherryvale Kansas. The proposed locations for sampling are depicted in Figure 1

The sample strategy and purpose is articulated in the above-referenced plan. The objective is to collect sufficient sample mass at several locations to evaluate the relative bioavailability of metals in soils in the sample areas. The number and distribution of samples is generally discussed in the Removal Site Evaluation Work Plan for Phase I Testing that outlines the approach for bioaccessibility testing of the site soils.

Work will be performed by field technicians familiar with the project objectives and experienced with soil sampling. Level D personal protective equipment (PPE) will be used during field activities and will consist of the following items: Steel-toed boots, nitrile gloves, appropriate work wear, and eye protection.

Pre-Sampling Activities

- The Respondents intend to seek access to the sites for sampling from the tenants and landowners of record. Crews will be mobilized to stake sample locations following receipt of written approval by the land owner or tenant. Because the samples will be collected from the surface using hand tools, utility clearances will not be performed.

Sample Locations

- Sample locations will initially be identified on the ground and marked for sample collection in the areas depicted in Figure 1. The specific sample locations may be adjusted in the field depending on access and actual field conditions.
- In-field X-ray fluorescence (XRF) analysis may be performed at select locations to obtain qualitative information regarding soil lead levels which can be used to guide sample collection. The criteria selected is in the range of 200 mg/kg lead. Screening will be performed directly on the soil surface, as-collected sample aliquots and composites as appropriate. XRF screening is not designed for removal assessment. An Innov-X Alpha portable X-ray fluorescence analyzer operating in soil mode, will be used for sample screening in the field. The instrument is calibrated against NIST traceable standards and will be operated as per the manufacturer's instructions. Operators will be trained in the proper use of the instrument and will have the

applicable license and certifications from KDHE for use of portable X-ray equipment in Kansas.

- Samples will be collected away from building drip lines.
- Samples will be collected from soils impacted by apparent smelter waste materials at a depth from 0 to 2 cm from the soil surface. The pre-sieve target volume will be at least 350 cc or as much soil material as needed to obtain a minimum of 10 grams of -250 micron fraction soils after sieving.
- In areas designated for screening for historical aerial deposition, the samples will be collected from below the grass layer if present. The grass layer will be peeled back with hand tools to expose the underlying soil immediately below the grass root zone and the 2 cm sample collected from this layer.

Soil Sampling

- The samples will be identified by street address or geographic area with a sequential number designated for each sample and composite. Locations will be noted on maps so the samples and composites can be easily identified.
- Using clean stainless steel or plastic instruments, sample aliquots will be collected at 3 points from each subject location from within 2 cm of the soil surface.
- Equal volumes of the three bulk subsamples will be collected from each of the target areas will be homogenized and composited into a single sample. Rock fragments, organic material or debris greater than approximately 1 cm will be removed from the sample composite, however, the sample will not be dried or sieved in the field to recover the fine fraction. Some oversized suspected smelter waste may be included in the sample which will be sieved out at the laboratory and used for source material characterization.
- Samples for analysis will be placed in either laboratory supplied jars or plastic bags for shipment to the laboratory depending on field conditions.
- Sample tools and containers will be cleaned between locations with distilled water and phosphate-free detergent.
- Excess sample aliquots and wash water will remain on the property where the sample was collected. Any sample hole or depression will be covered with excess sample material.
- Disposable equipment and PPE remaining from the sampling activity will be cleaned of loose material and bagged for disposal.

- Sample locations, physical observations of soil conditions, photographs, and other pertinent information will be recorded and sample locations will be spotted using scaled map sketches and portable GPS.
- Samples will be shipped in iced coolers with appropriate chain of custody to Dr. John Drexler at the Laboratory for Environmental and Geochemical Studies (LEGS) at the University of Colorado at Boulder, via commercial carrier from Independence, Kansas.

Post-Sampling Activity

Field data and results will be recorded and compiled into maps and tables following completion of the work and a summary report will be prepared for review by KDHE.

The sample collection work will be performed by staff and contractors on behalf of the Respondents under the supervision of Mark Landress, Kansas Licensed Professional Geologist No. 793. Project Navigator, Ltd. KDHE 2013 Radiation Machine Certificate of Registration No. 7192.

Figure 1
KDHE Cherryvale, KS
Surface Soil
Investigation

Bioavailability
Sample Locations



Legend

- Ditch Sample
- Adjacent to Sidewalk
- Ball Field & Logan Park
- Apparent Residential Slag
- Apparent Aerial Deposition
- Ditch Structure
- Sidewalk

Note:
 Aerial source: Google Earth
 Locations approximate



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Exhibit B

Standard Operating Procedure: *In Vitro* Bioaccessibility Assay for Lead in Soil





Standard Operating Procedure for an *In Vitro* Bioaccessibility Assay for Lead in Soil

1.0 Scope and Application

The purpose of this standard operating procedure (SOP) is to define the proper analytical procedure for the validated *in vitro* bioaccessibility assay for lead in soil (U.S. EPA, 2007b), to describe the typical working range and limits of the assay, and to indicate potential interferences. At this time, the method described herein has only been validated for lead in soil (U.S. EPA, 2007b).

The SOP described herein is typically applicable for the characterization of lead bioaccessibility in soil. The assay may be varied or changed as required and dependent upon site conditions, equipment limitations, or limitations imposed by the procedure. Users are cautioned that deviations in the method from the assay described herein may impact the results (and the validity of the method). Users are strongly encouraged to document any deviations as well as the comparison and associated Quality Assurance (QA) in any report.

This document is intended to be used as reference for developing site-specific Quality Assurance Project Plans (QAPPs) and Sampling and Analysis Plans (SAPs), but not intended to be used as a substitute for a site-specific QAPP or a detailed SAP.

Mention of trade names or commercial products does not constitute endorsement or recommended use by U.S. EPA.

2.0 Method Summary

Reliable analysis of the potential hazard to children from ingestion of lead in the environment depends on accurate information on a number of key parameters, including (1) lead concentration in environmental media (soil, dust, water, food, air, paint, etc.), (2) childhood intake rates of each medium, and (3) the rate and extent of lead absorption from each medium ("bioavailability"). Knowledge of lead bioavailability is important because the amount of lead that actually enters the body from an ingested medium depends on the physical-chemical properties of the lead and of the medium. For example, lead in soil may exist, at least in part, as poorly water-soluble minerals, and may also exist inside particles of inert matrix such as rock or slag of variable size, shape, and association. These chemical and physical properties may tend to influence (usually decrease) the absorption (bioavailability) of lead when ingested. Thus, equal ingested doses of different forms of lead in different media may not be of equal health concern.

The bioavailability of lead in a particular medium may be expressed either in absolute terms (absolute bioavailability) or in relative terms (relative bioavailability).

- Absolute Bioavailability (ABA) is the ratio of the amount of lead absorbed compared to the amount ingested:

$$\text{ABA} = (\text{Absorbed Dose}) / (\text{Ingested Dose})$$

This ratio is also referred to as the oral absorption fraction (AFo).

- Relative Bioavailability (RBA) is the ratio of the absolute bioavailability of lead present in some test material compared to the absolute bioavailability of lead in some appropriate reference material:

$$\text{RBA} = \text{ABA}(\text{test}) / \text{ABA}(\text{reference})$$

For example, if 100 µg of lead contained in soil were ingested and 30 µg entered the body, the ABA for soil would be:

$$30 (\text{Absorbed Dose}) / 100 (\text{Ingested Dose}), \text{ or } 0.30 (30\%).$$

Likewise, if 100 micrograms (µg) of lead dissolved in drinking water were ingested and a total of 50 µg entered the body, the ABA would be:

$$50 (\text{Absorbed Dose}) / 100 (\text{Ingested Dose}), \text{ or } 0.50 (50\%).$$

If the lead dissolved in water was used as the frame of reference for describing the relative amount of lead absorbed from soil, the RBA would be:

$$0.30 (\text{test}) / 0.50 (\text{reference}), \text{ or } 0.60 (60\%).$$

Usually the form of lead used as reference material is a soluble compound such as lead acetate that is expected to completely dissolve when ingested.

The *in vitro* bioaccessibility assay described in this SOP provides a rapid and relatively inexpensive alternative to *in vivo* assays for predicting RBA of lead in soils and soil-like materials. The method is based on the concept that lead solubilization in gastrointestinal fluid is likely to be an important determinant of lead bioavailability *in vivo*. The method measures the extent of lead solubilization in an extraction solvent that resembles gastric fluid. The fraction of lead which solubilizes in an *in vitro* system is referred to as *in vitro* bioaccessibility (IVBA), which may then be used as an indicator of *in vivo* RBA. Measurements of IVBA using this assay have been shown to be a reliable predictor of *in vivo* RBA of lead in a wide range of soil types and lead phases from a variety of different sites (U.S. EPA, 2007b).

3.0 Sample Preparation, Preservation, Containers, Handling, and Storage

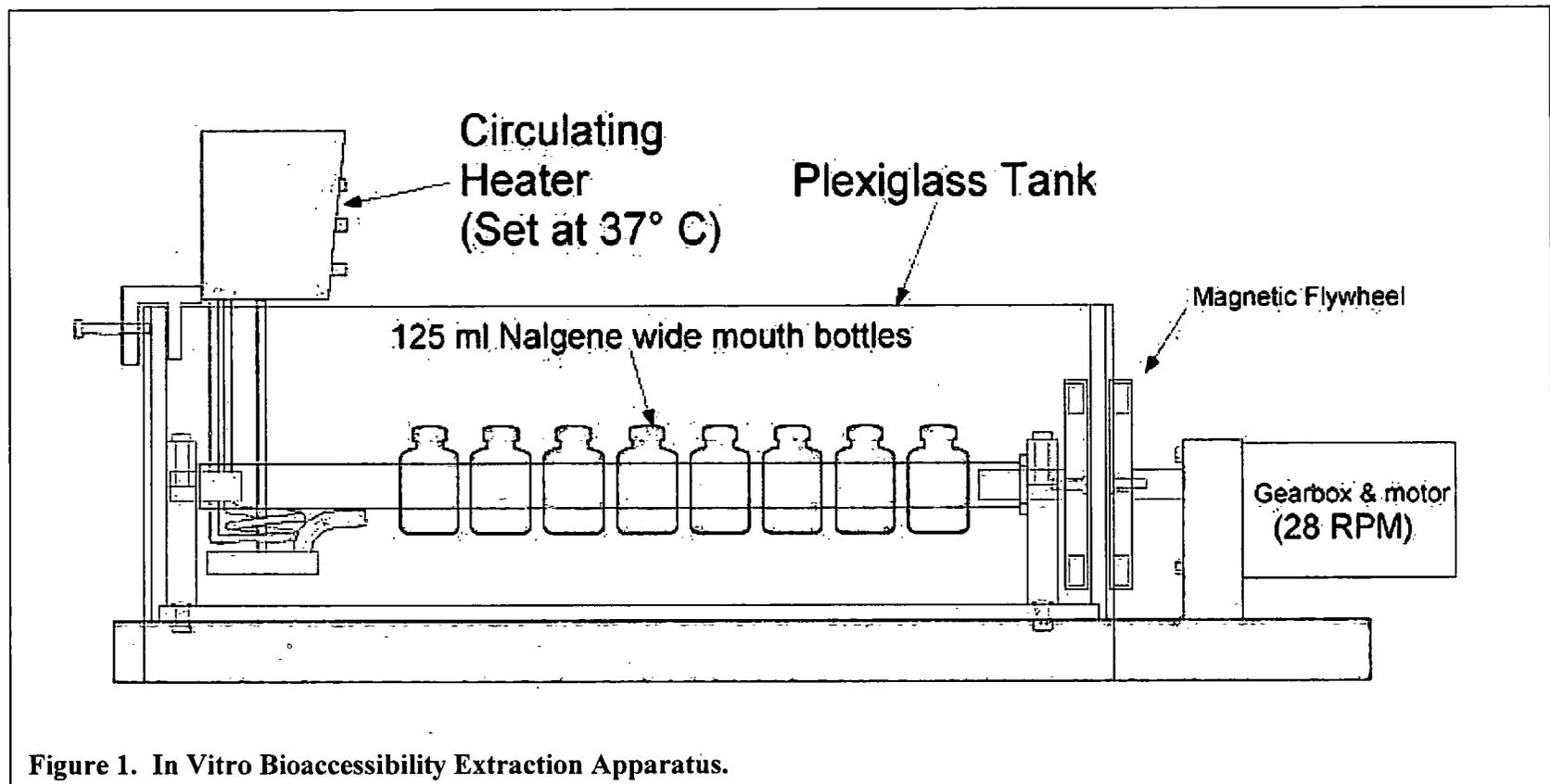
All test soils should be prepared by drying (<40°C) and sieving to <250 µm. The <250 µm size fraction was used because this particle size is representative of that which adheres to children's hands (U.S. EPA, 2000). Stainless steel sieves are recommended. Samples should be thoroughly mixed prior to use to ensure homogenization. Mixing and aliquoting of samples using a riffle splitter is recommended. Clean plastic bags or storage bottles are recommended. All samples should be archived after analysis and retained for further analysis for a period of six (6) months. No preservatives or special storage conditions are required.

4.0 Interferences and Potential Problems

At present, it appears that the relationship between IVBA and RBA is widely applicable, having been found to hold true for a wide range of different soil types and lead phases from a variety of different sites. However, the majority of the samples tested have been collected from mining and milling sites, and it is plausible that some forms of lead that do not occur at this type of site might not follow the observed correlation. Thus, whenever a sample containing an unusual and/or untested lead phase is evaluated by the IVBA protocol, this sample should be identified as a potential source of uncertainty. In the future, as additional samples with a variety of new and different lead forms are tested by both *in vivo* and *in vitro* methods, the applicability of the method will be more clearly defined. In addition, excess phosphate in the sample medium may result in interference (i.e., the assay is not suited to phosphate-amended soils). Interferences and potential problems are discussed under Procedures (Section 7).

5.0 Apparatus

The main piece of equipment used for this procedure is the extraction device shown in Figure 1. An electric motor (the same motor as is used in the Toxicity Characteristic Leaching Procedure, or TCLP) drives a flywheel, which in turn drives a Plexiglass block situated inside a temperature-controlled water bath. The Plexiglass block contains ten 5-centimeter holes with stainless steel screw clamps, each of which is designed to hold a 125-mL wide-mouth high density polyethylene (HDPE) bottle. The water bath should be filled such that the extraction bottles are completely immersed. Temperature in the water bath should be maintained at 37±2 °C using an immersion circulator heater. The 125-mL HDPE bottles should have air-tight screw-cap seals, and care should be taken to ensure that the bottles do not leak during the extraction procedure. All equipment should be properly cleaned, acid washed, and rinsed with deionized water prior to use.



6.0 Reagents

All reagents should be free of lead and the final fluid should be tested to confirm that lead concentrations are $< \frac{1}{4}$ ($<$ one-fourth) the project required detection limit (PRDL) of 10 $\mu\text{g/L}$ (i.e., $< 2 \mu\text{g/L}$ lead in the final fluid). Cleanliness of all materials used to prepare and/or store the extraction fluid and buffer is essential; all glassware and equipment used to prepare standards and reagents should be properly cleaned, acid washed, and triple-rinsed with deionized water prior to use.

7.0 Procedures

The dissolution of lead from a test material into the extraction fluid depends on a number of variables including extraction fluid composition, temperature, time, agitation, solid/fluid ratio, and pH. Any alterations in these parameters should be evaluated to determine the optimum values for maximizing sensitivity, stability, and the correlation between *in vitro* and *in vivo* values. Additional discussion of these procedures is available in U.S. EPA (2007b) and Drexler and Brattin (2007).

7.1 Extraction Fluid

The extraction fluid for this procedure is 0.4 M glycine (free base, reagent grade glycine in deionized water), adjusted to a pH of 1.50 ± 0.05 at 37°C using trace metal grade concentrated hydrochloric acid (HCl).¹

7.2 Temperature

A temperature of 37°C should be used because this is approximately the temperature of gastric fluid *in vivo*.

7.3 Extraction Time

The time that ingested material is present in the stomach (i.e., stomach-emptying time) is about 1 hour for a child, particularly when a fasted state is assumed (see U.S. EPA 2007a, Appendix A). Thus, an extraction time of 1 hour should be used. It was found that allowing the bottles to stand at room temperature for up to 4 hours after rotation at 37°C caused no significant variation ($< 10\%$) in lead concentration.

7.4 pH

Human gastric pH values tend to range from about 1 to 4 during fasting (see U.S. EPA 2007b, Appendix A). For the IVBA, a pH of 1.5 should be used.

¹ Most previous *in vitro* test systems have employed a more complex fluid intended to simulate gastric fluid. For example, Medlin (1997) used a fluid that contained pepsin and a mixture of citric, malic, lactic, acetic, and hydrochloric acids. When the bioaccessibility of a series of test substances were compared using 0.4 M glycine buffer (pH 1.5) with and without the inclusion of these enzymes and metabolic acids, no significant difference was observed ($p=0.196$). This indicates that the simplified buffer employed in the procedure is appropriate, even though it lacks some constituents known to be present in gastric fluid.

7.5 Agitation

If the test material is allowed to accumulate at the bottom of the extraction apparatus, the effective surface area of contact between the extraction fluid and the test material may be reduced, and this may influence the extent of lead solubilization. Depending on which theory of dissolution is relevant (Nernst and Brunner, 1904, or Dankwerts, 1951), agitation will greatly affect either the diffusion layer thickness or the rate of production of fresh surface. Previous workers have noted problems associated with both stirring and argon bubbling methods (Medlin and Drexler, 1995; Drexler, 1997). Although no systematic comparison of agitation methods was performed, an end-over-end method of agitation is recommended.

7.6 Solid/Fluid Ratio and Mass of Test Material

A solid-to-fluid ratio of 1/100 (mass per unit volume) should be used to reduce the effects of metal dissolution as noted by Sorenson *et al.* (1971) when lower ratios (1/5 and 1/25) were used. Tests using Standard Reference Materials (SRM 2710a) showed no significant variation (within $\pm 1\%$ of control means) in the fraction of lead extracted with soil masses as low as 0.2 gram (g) per 100 mL. However, use of low masses of test material could introduce variability due to small scale heterogeneity in the sample and/or to weighing errors. Therefore, the final method employs 1.0 g of test material in 100 mL of extraction fluid.

In special cases, the mass of test material may need to be < 1.0 g to avoid the potential for saturation of the extraction solution. Tests performed using lead acetate, lead oxide, and lead carbonate indicate that if the bulk concentration of a test material containing these relatively soluble forms of lead exceed approximately 50,000 ppm, the extraction fluid becomes saturated at 37°C and, upon cooling to room temperature and below, lead chloride crystals will precipitate. To prevent this from occurring, the concentration of lead in the test material should not exceed 50,000 ppm, or the mass of the test material should be reduced to 0.50 ± 0.01 g.

7.7 Summary of Final Leaching Protocol

The extraction procedure is begun by placing 1.00 ± 0.05 g of sieved test material ($< 250 \mu\text{m}$) and 100 ± 0.5 mL of the buffered extraction fluid (0.4 M glycine, pH 1.5) into a 125-mL wide-mouth HDPE bottle. Care should be taken to ensure that static electricity does not cause soil particles to adhere to the lip or outside threads of the bottle; if necessary, an antistatic brush can be used to eliminate static electricity prior to adding the test substrate. The bottle should be tightly sealed and then shaken or inverted to ensure that there is no leakage and that no soil is caked on the bottom of the bottle.

Each bottle should be placed into the modified TCLP extractor (water temperature $37 \pm 2^\circ\text{C}$). Samples are extracted by rotating the samples end-over-end at 30 ± 2 rpm for 1 hour. After 1 hour, the bottles should be removed, dried, and placed upright on the bench top to allow the soil to settle to the bottom. A 15-mL sample of supernatant fluid is removed directly from the extraction bottle into a disposable 20-cc syringe. After withdrawal of the sample into the syringe, a Luer-Lok attachment fitted with a $0.45\text{-}\mu\text{m}$ cellulose acetate disk filter (25 mm diameter) is attached, and the 15 mL aliquot of fluid is filtered through the attachment to remove any particulate matter. This filtered sample of extraction fluid is then analyzed for lead, as

described below. If the total time elapsed for the extraction process exceeds 90 minutes, the test must be repeated.

As noted above, in some cases (mainly slag soils), the test material can increase the pH of the extraction buffer, and this could influence the results of the bioaccessibility measurement. To guard against this, the pH of the fluid should be measured at the end of the extraction step (just after a sample was withdrawn for filtration and analysis). If the pH is not within 0.5 pH units of the starting pH (1.5), the sample should be re-analyzed. If the second test also resulted in an increase in pH of >0.5 units, it is reasonable to conclude that the test material is buffering the solution. In these cases, the test should be repeated using manual pH adjustment during the extraction process, stopping the extraction at 5, 10, 15, and 30 minutes and manually adjusting the pH down to pH 1.5 at each interval by drop-wise addition of HCl.

7.8 Analysis of Extraction Fluid for Lead

The filtered samples of extraction fluid should be stored in a refrigerator at 4°C until they are analyzed (within 1 week of extraction). Once received by the laboratory, all media should be maintained under standard chain-of-custody. The samples should be analyzed for lead by ICP-AES or ICP-MS (U.S. EPA Method 6010 or 6020, U.S. EPA, 1986). The method detection limit (MDL) in extraction fluid should be approximately 20 µg/L for Method 6010 and 0.1-0.3 µg/L for Method 6020.

8.0 Calculations

In order for an *in vitro* bioaccessibility test system to be useful in predicting the *in vivo* RBA of a test material, it is necessary to establish empirically that a strong correlation exists between the *in vivo* and the *in vitro* results across many different samples. Because there is measurement error not only in RBA but also in IVBA, linear fitting was also performed taking the error in both RBA and IVBA into account. There was nearly no difference in fit, so the results of the weighted linear regression were selected for simplicity (U.S. EPA, 2007b). This decision may be revisited as more data become available. Based on this decision, the currently preferred model is:

$$\text{RBA} = 0.878 \cdot \text{IVBA} - 0.028$$

It is important to recognize that use of this equation to calculate RBA from a given IVBA measurement will yield the “typical” RBA value expected for a test material with that IVBA, and the true RBA may be somewhat different (either higher or lower).

9.0 Quality Control/Quality Assurance

Recommended quality assurance for the extraction procedure are as follows:

- Reagent Blank — extraction fluid analyzed once per batch.
- Bottle Blank — extraction fluid only (no test soil) run through the complete procedure at a frequency of 1 in 20 samples (minimum of 1 per batch).

- Blank Spike — extraction fluid spiked at 10 mg/L lead, and run through the complete procedure at a frequency of 1 in 20 samples (minimum of 1 per batch).
- Matrix Spikes — subsample of each material used for duplicate analyses used as a matrix spike. The matrix spike should be prepared at 10 mg/L lead and run through the extraction procedure at a frequency of 1 in 10 samples (minimum of 1 per batch).
- Duplicate Sample — duplicate sample extractions performed on 1 in 10 samples (minimum of 1 per batch).
- Control Soil — National Institute of Standards and Testing (NIST) Standard Reference Material (SRM) 2711 (Montana Soil) used as a control soil. The SRM should be analyzed at a frequency of 1 in 20 samples (minimum 1 per batch).

Recommended control limits for these quality control samples:

Analysis	Frequency	Control Limits
Reagent blank	once per batch	<25 µg/L lead
Bottle blank	5%*	<50 µg/L lead
Blank spike (10 mg/L)	5%*	85-115% recovery
Matrix spike (10 mg/L)	10%*	75-125% recovery
Duplicate sample	10%*	±20% RPD
Control soil (NIST 2711)	5%*	±10% RPD

RPD = Relative percent difference

*Minimum of once per batch

10.0 Data Validation

NIST SRM 2711 should be used as a control soil. To evaluate the precision of the *in vitro* bioaccessibility extraction protocol, replicate analyses of standard reference materials (NIST SRM 2710 or 2711) should be used. The SRM will be analyzed at a frequency of 1 in 20 samples (minimum 1 per batch).

11.0 Health and Safety

When working with potentially hazardous materials, follow U.S. EPA, OSHA, or corporate health and safety procedures.

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Exhibit C

Standard Operating Procedure: Electron Microprobe Analysis



Speciation

EMPA-SOP

1.0 OBJECTIVES

The objectives of this Standard Operating Procedure (SOP) are to specify the proper methodologies and protocols to be used during metal speciation of various solid samples including; tailings, slags, sediments, dross, bag house dusts, wipes, paint, soils, and dusts for metals. The metal speciation data generated from this SOP may be used to assess the solid samples as each phase relates to risk. Parameters to be characterized during the speciation analyses include particle size, associations, stoichiometry, frequency of occurrence of metal-bearing forms and relative mass of metal-bearing forms. This electron microprobe (EMPA) technique, instrument operation protocols and sample preparation to be used during implementation of the Metals Speciation SOP are discussed in the following sections.

2.0 BACKGROUND

To date, numerous metal-bearing forms of soils have been identified from various environments within western mining districts (Emmons et al., 1927; Drexler, 1991 per. comm.; Drexler, 1992; Davis et al., 1993; Ruby et al., 1994; CDM, 1994; WESTON, 1995). This listing does not preclude the identification of other metal-bearing forms, but only serves as an initial point of reference. Many of these forms are minerals with varying metal concentrations (e.g., lead phosphate, iron-lead oxide, and slag). Since limited thermodynamic information is available for many of these phases and equilibrium conditions are rarely found in soil environments, the identity of the mineral class (e.g., lead phosphate) will be sufficient and exact stoichiometry is not necessary.

It may be important to know the particle-size distribution of metal-bearing forms in order to assess potential risk. It is believed that particles less than 250 microns (μm) are most available for human ingestion and/or inhalation (Bornschein, et al., 1987). For this study, the largest dimension of any one metal-bearing form will be measured and the frequency of occurrence weighted by that dimension. Although not routinely performed, particle area can be determined, it has been shown (CDM, 1994) that data collected on particle area produces similar results. These measurements add a considerable amount of time to the procedure, introduce new sources of potential error and limit the total number of particles or samples that can be observed in a study.

Mineral association may have profound effects on the ability for solubilization. For example, if a lead-bearing form in one sample is predominantly found within quartz grains while in another sample it is free in the sample matrix, the two samples are likely to pose significantly different risk levels to human health.

Therefore, associations of concern include the following:

1. free or liberated
2. inclusions within a second phase
3. cementing rimming

3.0 SAMPLE SELECTION

Samples should be selected and handled according to the procedure described in the Project Plan. Unless help in determination of sample selection and frequency is requested by the client it is their responsibility to

provide a “representative” number of samples to the laboratory for analyses.

4.0 SCHEDULE

A schedule for completion of projects performed under this Metals Speciation SOP will be provided in writing or verbally to the contractor along with monthly reporting requirements if large projects are performed. These schedules are based on an aggressive analytical program designed to ensure that the metals speciation analyses are completed in a timely period. Monthly reports are expected to reflect schedule status.

5.0 INSTRUMENTATION

Speciation analyses will be conducted at the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado, Boulder or other comparable facilities. Primary equipment used for this work will include:

Electron Microprobe (JEOL 8600) equipped with four wavelength spectrometers, energy dispersive spectrometer (EDS), BEI detector and the Geller, dQuant data processing system. Geller dPict hardware may be used for image storage and processing. An LEDC spectrometer crystal for carbon and LDE-1 crystal for oxygen analyses are essential.

6.0 PRECISION AND ACCURACY

The precision of the EMPA speciation will be evaluated based on sample duplicates analyzed at a frequency of 10% as selected by the laboratory, however the client may also submit “blind” duplicates for analyses. The precision of the data generated by the “EMPA point count” will be evaluated by calculating RPD values for all major (>20% frequency) phases, comparing the original result with the duplicate result. If the duplicate analyses are from samples that have produced at least 100 total particles it is expected that all (100%) of the dominant species (representing 60% of frequency) be found in both, and that their individual frequency of occurrence not vary by more than 30% , relative. In the evaluation of the method precision it is most important to consider the variation in results among all samples studied for a particular media, since the overall particle count is very large Data generated by the “EMPA point count” will be further evaluated statistically based on the methods of Mosimann (1965) at the 95% confidence level on the frequency data following Equation 1.

$$E_{0.95} = 2P(100-P)/N$$

Where: $E_{0.95}$ = Probable error at the 95% confidence level

P = Percentage of N of an individual metal-bearing phase based on percent length frequency

N = Total number of metal-bearing grains counted

Accuracy of quantitative metal analyses on non-stoichiometric metal phases is based on established EMPA procedures, and data reduction, Heinrich, 1981 and is generally 1-2% relative. All quantitative analyses will be performed using a series of certified mineral standards. In general, site-specific concentrations for these variable, metal-bearing forms will be determined by performing “peak counts” on the appropriate wavelength spectrometer. Average concentrations will then be used for further calculations. Data on specific gravity will be collected from referenced databases or estimated based on similar compounds.

7.0 PERSONNEL RESPONSIBILITY

The analysts will carefully read this SOP prior to any sample examination.

It is the responsibility of the laboratory supervisor and designates to ensure that these procedures are followed, to examine quality assurance (QA) samples and replicate standards, and to check EDS and WDS calibrations. The laboratory supervisor will collect results, ensure they are in proper format, and deliver them to the contractor.

Monthly reports summarizing all progress, with a list of samples speciated to date with data analyses sheets (DAS), will be submitted each month.

It is also the responsibility of the laboratory supervisor to notify the contractor representative of any problems encountered in the sample analysis process.

8.0 SAMPLE PREPARATION

Grain mounts (1.5 inches in diameter) of each sample will be prepared using air-cured epoxy. Previous work (CDM, 1994, Weston, 1995) found that neither using mono-layer mounts nor repetitive exposure of deeper layers within the epoxy puck produced speciation results outside those errors observed from single sample duplicates. Once a sample is well stirred within the epoxy minimal settling was observed. This grain mounting technique is appropriate for most speciation projects, however polished thin-sections, paint chips, dust wipes, or filters may be prepared in a similar manner. The grain mounting is performed as follows:

1. Log the samples for which polished mounts will be prepared.
2. Inspect all disposable plastic cups, making sure each is clean and dry.
3. Label each "mold" with its corresponding sample number.
4. All samples will be split to produce a homogeneous 1-4 gram sample.
5. Mix epoxy resin and hardener according to manufacturer's directions.
6. Pour 1 gram of sample into mold. Double check to make sure sample numbers on mold and the original sample container match. Pour epoxy into mold to just cover sample grains.
7. Use a new wood stirring stick with each sample, carefully blend epoxy and grains so as to coat all grains with epoxy.
8. Set molds to cure at ROOM TEMPERATURE in a clean restricted area. Add labels with sample numbers and cover with more epoxy resin. Leave to cure completely at room temperature.
9. One at a time remove each sample from its mold and grind flat the back side of the mount.
10. Use 600 grit wet abrasive paper stretched across a grinding wheel to remove the bottom layer and expose as many mineral grains as possible. Follow with 1000 grit paper.
11. Polish with 15 um oil-based diamond paste on a polishing paper fixed to a lap. Use of paper instead of cloth minimizes relief.
12. Next use 6um diamond polish on a similar lap.
13. Finally polish the sample with 1um oil-based diamond paste on polishing paper, followed by 0.05 um alumina in water suspension. The quality should be checked after each step. Typical polishing times are 30 minutes for 15 um, 20 minutes for 6 um, 15 minutes for 1 um, and 10 minutes for 0.05 um.

NOTE: use low speed on the polishing laps to avoid "plucking" of sample grains.

14. Samples should be completely cleaned in an ultrasonic cleaner with isopropyl alcohol or similar solvent to remove oil and fingerprints.
15. To ensure that no particles of any metal are being cross-contaminated during sample preparation procedures, a blank (epoxy only) mold will be made every 20th sample (5% of samples) following all of the above procedures. This mold will then be speciated along with the other samples.

16. Each sample must be carbon coated. Once coated, the samples should be stored in a clean, dry environment with the carbon surface protected from scratches or handling.

9.0 GEOCHEMICAL SPECIATION USING ELECTRON MICROPROBE

All investigative samples will also be characterized using EMPA analysis to determine the chemical speciation, particle size distribution and frequency for several target metals.

10.1 Concentration Prescreening

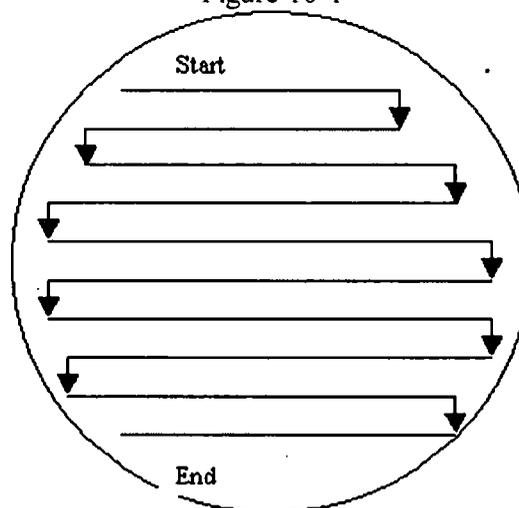
All samples will be initially examined using the electron microprobe to determine if the number of particles are too great to obtain a representative count. The particle counting will be considered representative if the entire sample (puck) has been traversed about the same time in which the counting criteria are achieved.

If this examination reveals that one metal is highly abundant ($> 10,000$ mg/kg in concentration), clean quartz sand (SiO_2) will be mixed with the sample material. The sand should be certified to be free of target analytes. The quartz sand should be added to an aliquot of the investigative sample, then mixed by turning the sample for a minimum of one hour, or until the sample is fully homogenized. The initial mass of the investigative sample aliquot, and the mass of the quartz addition must be recorded on the Data Analysis Sheet (DAS).

10.2 Point Counting

Counts are made by traversing each sample from left-to-right and top-to-bottom as illustrated in Figure 10-1. The amount of vertical movement for each traverse would depend on magnification and CRT (cathode-ray tube) size. This movement should be minimized so that NO portion of the sample is missed when the end of a traverse is reached. Two magnification settings generally are used. One ranging from 40-100X and a second from 300-500X. The last setting will allow one to find the smallest identifiable (1-2 micron) phases.

Figure 10-1



The portion of the sample examined in the second pass, under the higher magnification, will depend on the time available, the number of metal-bearing particles, and the complexity of metal mineralogy. A maximum of 8 hours will be spent on each analysis or a total particle count of 100.

The point counting procedure in petrography is a well established technique as outlined by Chayes, 1949. For our procedure we have simply substituted the electron microprobe for a simple petrographic microscope as a

means of visually observing a particle and identifying its composition using the attached x-ray analyzers. The operator error (identification of phase and sizing) is generally negligible. However the particle counting error can be significant depending on the total number of particles counted and the individual component (species) percent. Based on studies in El-Hinnawi, 1966, it was shown that the relative error of a point count based on 100 total particles versus one of 300 total particles is only 10% and 6% , respectively (for a species representing 30% of the count). It is our belief that this small decrease in error is not justified when cost and time of analysis are considered, and that it is much more beneficial to increase your total sample population and address representativeness.

10.3 Data Reduction

Analysts will record data as they are acquired from each sample using the LEGS software (10-3), which places all data in a spreadsheet file format. Columns have been established for numbering the metal-bearing phase particles, their identity, size of longest dimension in microns, along with their association (L = liberated, C= cementing, R = rimming, I = included) (10-2). The analyst may also summarize his/her observations in the formatted data summary files.

The frequency of occurrence and relative metal mass of each metal-bearing form as it is distributed in each sample will be depicted graphically as a frequency bar-graph (10-5). The particle size distribution of metal-bearing forms will be depicted in a histogram. Size-histograms of each metal-bearing form can be constructed from data in the file.

Data from EMPA will be summarized using two methods. The first method is the determination of FREQUENCY OF OCCURRENCE. This is calculated by summing the longest dimension of all the metal-bearing phases observed and then dividing each phase by the total.

Equation 2 will serve as an example of the calculation.

$$F_M \text{ in phase-1} = \frac{\Sigma(\text{PLD})_{\text{phase 1}}}{\Sigma(\text{PLD})_{\text{phase-1}} + \Sigma(\text{PLD})_{\text{phase-2}} + \Sigma(\text{PLD})_{\text{phase-n}}}$$

Where:

F_M = Frequency of occurrence of metal in a single phase.

PLD = An individual particle's longest dimension.

$\%F_M \text{ in phase-1} = F_M \text{ in phase-1} * 100$

These data thus illustrate which metal-bearing phase(s) are the most commonly observed in the sample or relative volume percent.

The second calculation used in this report is the determination of RELATIVE METAL MASS. These data are calculated by substituting the PLD term in the equation above with the value of MM. This term is calculated as defined below.

$$M_M = F_M * SG * \text{ppm}_M$$

Where:

M_M = Mass of metal in a phase

SG = Specific Gravity of a phase

ppm_M = Concentration in ppm of metal in a phase

The advantage in reviewing the RELATIVE METAL MASS determination is that it gives one information as to which metal-bearing phase(s) in a sample are likely to control the total bulk concentration for a metal of interest. For example, PHASE-1 may comprise 98% relative volume of the sample; however, it has a low specific gravity and contains only 1,000 parts per million (ppm) arsenic. PHASE-2 comprised 2% of the sample, has a high specific gravity, and contains 850,000 ppm of arsenic. In this example it is PHASE-2 that is the dominant source of arsenic to the sample.

Finally, a concentration for each phase is calculated. This quantifies the concentration of each metal-bearing phase. This term is calculated as defined below (Eq. 4).

$$\text{ppm}_M = M_M * \text{Bulk metal concentration in ppm}$$

10.4 Analytical Procedure

A brief visual examination of each sample will be made, prior to EMPA examination. This examination may help the operator by noting the occurrence of slag and/or organic matter. Standard operating conditions for quantitative and qualitative analyses of most metal-bearing forms are given in Figure 10-4. However, it is the responsibility of the operator to select the appropriate analytical line (crystal/KeV range) to eliminate peak overlaps and ensure proper identification/quantification of each analyte. Quality control will be maintained by analyzing duplicates at regular intervals (Section 6).

The backscattered electron threshold will be adjusted so that all particles in a sample are seen. This procedure will minimize the possibility that low metal-bearing minerals may be overlooked during the scanning of the polished grain mount. The scanning will be done manually in a manner similar to that depicted in Figure 10-1. Typically, the magnification used for scanning all samples except for airborne samples will be 40-100X and 300-600X. The last setting will allow the smallest identifiable (1-2 um) phases to be found. Once a candidate particle is identified, then the backscatter image will be optimized to discriminate any different phases that may be making up the particle or defining its association. Identification of the metal-bearing phases will be done using both EDS and WDS on an EMPA, with spectrometers typically peaked at sulfur, oxygen, carbon and the metal(s) of concern (M). The size of each metal-bearing phase will be determined by measuring in microns the longest dimension.

As stated previously, a maximum of 8 hours will be spent in scanning and analyzing each mount. For most speciation projects the goal is to count between 100-300 particles. In the event that these goals are achieved in less than 8 hours, particle counting may be stopped so the analyst may move to another sample in order to increase the sample population.

Quantitative Analyses

Quantitative analyses are required to establish the average metal content of the metal-bearing minerals, which have variable metal contents as: Iron-(M) sulfate, Iron-(M) oxide, Manganese-(M) oxide, organic, and slag. These determinations are important, especially in the case of slag, which is expected to have considerable variation in their dissolved metal content.

Results will be analyzed statistically to establish mean values. They may also be depicted as histograms to show the range of metal concentrations measured as well as the presence of one or more populations in terms of metal content. In the later case, non-parametric statistics may have to be used or the median value has to

be established.

Associations

The association of the metal-bearing forms will be established from the backscattered electron images. Particular attention will be paid in establishing whether the grains are totally enclosed, encapsulated or liberated. The rinds of metal-bearing grains will be identified. Representative photomicrographs of backscatter electron images establishing the association of the principal metal-bearing forms will be obtained for illustration purposes.

10.5 Instrument Calibration and Standardization

The WDS will have spectrometers calibrated for the metal of concern, carbon, oxygen and sulfur on the appropriate crystals using mineral standards. The EDS will have multi-channel analyzer (MCA) calibrated for known peak energy centroids. Calibration will be performed so as to have both low (1.0-3.0 KeV) and high (6.0-9.0 KeV) energy peaks fall within 0.05 KeV of its known centroid.

The magnification marker on the instrument will be checked once a week. This will be performed by following manufacturer instructions or by measurement of commercially available grids or leucite spheres. Size measurements must be within 4 microns of certified values.

Initial calibration verification standards (ICVs) must be analyzed at the beginning of each analytical batch or once every 48 hours, whichever is more frequent. A set of mineral or glass standards will be run quantitatively for the metal of concern, sulfur, oxygen and carbon. If elemental quantities of the ICVs do not fall within +/- 5% of certified values for each element, the instrument must be recalibrated prior to analysis of investigative samples.

The metal-bearing forms in these samples will be identified using a combination of EDS, WDS and BEI. Once a particle is isolated with the backscatter detector, a 5-second EDS spectra is collected and peaks identified. The count rates for the metal(s) of concern, sulfur, carbon and oxygen can be either visually observed on the wavelength spectrometers or K-ratios calculated.

10.6 Documentation

Photomicrographs along with EDS x-ray spectra should be taken for each sample, at a rate of 5% (1 photograph per 20 particles counted), or a minimum of 10 per sample and submitted with the results. Particles selected for photography must be recorded on the EMPA graph, as well as in the Electron Micrograph Logbook. Any additional photographs should be labeled as "opportunistic".

A 128x128 (minimum) binary image in ".tif" format may be stored. Recorded on each photomicrograph will be a scale bar, magnification, sample identification, date and phase identification. Abbreviations for the identified phases can be used. A final list must be submitted with the laboratory report.

10.0 PERSONAL HEALTH AND SAFETY

Each individual operating the electron microprobe instruments will have read the "Radiation Safety Handbook" prepared by the University and follow all State guidelines for operation of X-ray equipment.

Latex gloves and particulate masks will be worn during preparation of sample cups. All material that comes in contact with the samples or used to clean work surface areas will be placed in poly-bags for disposal.

11.0 FINAL REPORT

A final laboratory report will be provided to the Contractor. The report will include all EMPA data including summary tables and figures. Individual sample data will be provided on disk.

Speciation results will include: 1) a series of tables summarizing frequency of occurrence for each metal phase identified along with a confidence limit; 2) summary histograms of metal phases identified for each waste type; 3) a summary histogram of particle size distribution in each waste type; and 4) a summary of metal phase associations. Representative .tif images and EDS x-ray spectra will also be included in the final report.

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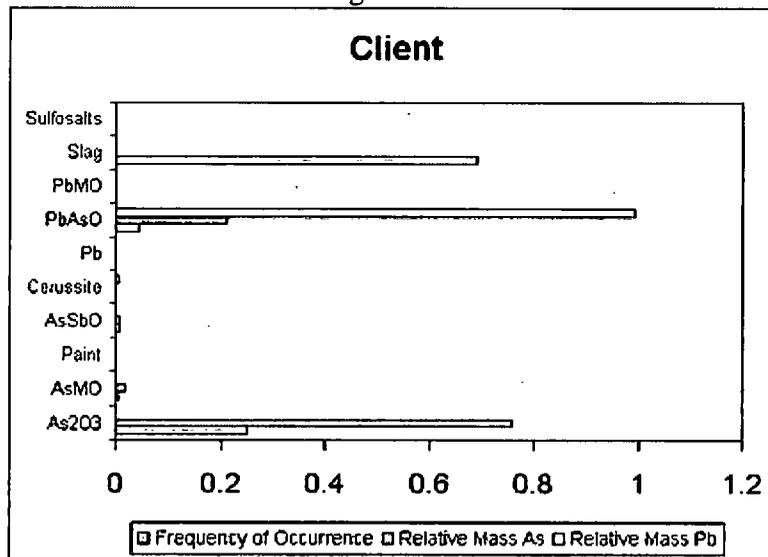
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Figure 10-2

NOTES	IDENTITY	SIZE	Liberated	Inclusions	ICemented	Rim
		Length-longest dimension (µm)				

Working Distance	N/A	Fixed
MCA Time Constant	N/A	7.5-12 microseconds
X-Ray Lines	S K-alpha PET O K-alpha LDE1 C K-alpha LDEC Zn K-alpha PET As L-alpha TAP Cu K-alpha LIF Cd L-alpha PET Pb M-alpha PET Pb L-alpha LIF In L-alpha PET Tl L-alpha LIF Hg L-alpha LIF Se L-alpha LIF Sb L-alpha PET	S K-alpha 2.31 KeV O K-alpha 0.52 KeV C K-alpha 0.28 KeV Pb M-alpha 2.34 KeV Pb L-alpha 10.5 KeV Zn K-alpha 8.63 KeV Cu K-alpha 8.04 KeV As K-alpha 10.5 KeV As L-alpha 1.28 KeV Cd L-alpha 3.13 KeV In L-alpha 3.28 KeV Tl M-alpha 2.27 KeV Tl L-alpha 10.26 KeV Hg L-alpha 9.98 KeV Hg M-alpha 2.19 KeV Se L-alpha 1.37 KeV Sb L-alpha 3.60 KeV

Figure 10-5



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