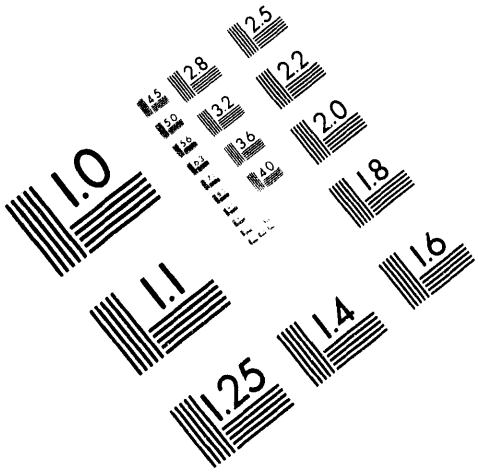

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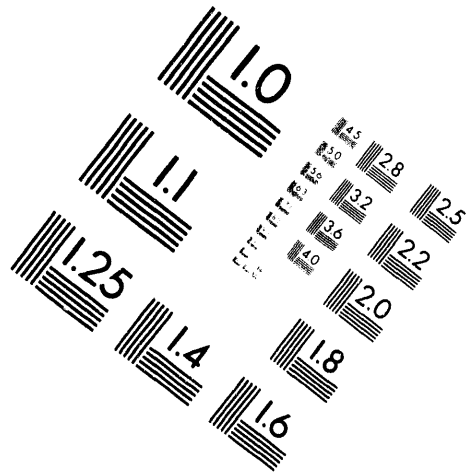

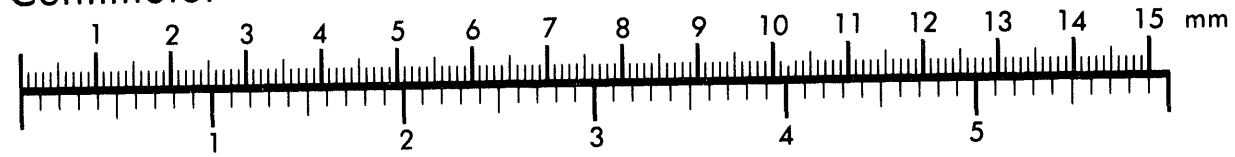

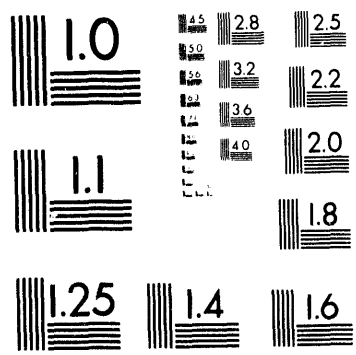

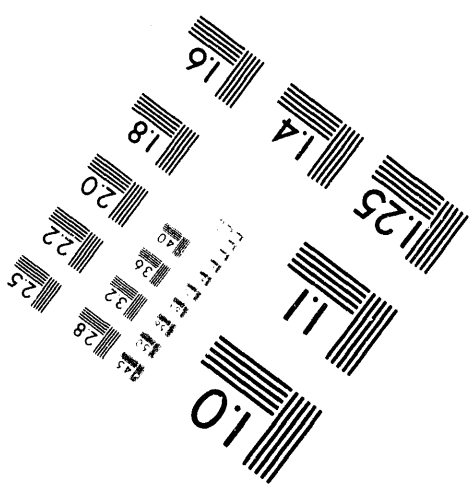

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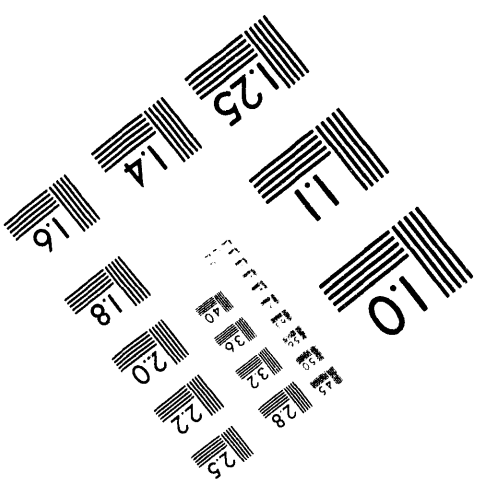

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The Development and Testing of Technologies for the Remediation of Mercury-Contaminated Soils
Task 7.52

Topical Report
December 1992 - December 1993

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February 1994

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EXECUTIVE SUMMARY

The release of elemental mercury into the environment from manometers that are used in the measurement of natural gas flow through pipelines has created a potentially serious problem for the gas industry. Regulations, particularly the Land Disposal Restrictions (LDR), have had a major impact on gas companies dealing with mercury-contaminated soils. After the May 8, 1993, LDR deadline extension, gas companies were required to treat mercury-contaminated soils by designated methods to specified levels prior to disposal in landfills. In addition, gas companies must comply with various state regulations that are often more stringent than the LDR. The gas industry is concerned that the LDRs do not allow enough viable options for dealing with their mercury-related problems.

The U.S. Environmental Protection Agency has specified the Best Demonstrated Available Technology (BDAT) as thermal roasting or retorting. However, the Agency recognizes that treatment of certain wastes to the LDR standards may not always be achievable and that the BDAT used to set the standard may be inappropriate. Therefore, a Treatability Variance Process for remedial actions was established (40 Code of Federal Regulations 268.44) for the evaluation of alternative remedial technologies.

This report presents evaluations of demonstrations for three different remedial technologies: a pilot-scale portable thermal treatment process, a pilot-scale physical separation process in conjunction with chemical leaching, and a bench-scale chemical leaching process.

THE DEVELOPMENT AND TESTING OF TECHNOLOGIES FOR THE REMEDIATION OF MERCURY-CONTAMINATED SOILS

1.0 INTRODUCTION

The Energy & Environmental Research Center (EERC) was contracted by the U.S. Department of Energy (DOE) and the Gas Research Institute (GRI) to investigate mercury contamination at gas industry sites. The mercury research program is part of a much broader multidisciplinary effort to investigate potential contamination to soil and groundwater at gas industry sites. This report summarizes work performed to evaluate the application of existing and developing remediation technologies for the mercury research program.

The release of elemental mercury into the environment from manometers used in the measurement of natural gas flow through pipelines has created a potentially serious problem for the gas industry. The manometers are most commonly located inside metering houses that often have earth floors. Contamination has resulted from leaky fittings, pressure surges, equipment failures, vandalism, and inadvertent spills during maintenance and servicing operations.

The area of contamination is generally confined to the soils inside the meter house or within a few feet of the door. The volume of contaminated material is typically 1 to 2 cubic meters per site. Although the amount of mercury-contaminated material at individual sites may not be large, there are thousands of sites of this type covering the entire country (Henke and others, 1993).

2.0 RATIONALE

Soils contaminated with mercury at gas metering sites may be subject to Resource Conservation and Recovery Act (RCRA) regulations if a sample of the excavated soil exceeds 0.2 mg/L of mercury as measured by the U.S. Environmental Protection Agency (USEPA) toxicity characteristic leaching procedure (TCLP). Mercury-contaminated soils that are determined to be hazardous by TCLP analysis are classified as D009 characteristic wastes and cannot be landfilled without meeting certain treatment standards.

D009 characteristic wastes are subdivided into a low-mercury category, with less than 260 mg/kg of total mercury, and a high-mercury category, with greater than 260 mg/kg of total mercury. D009 characteristic wastes containing less than 260 mg/kg of total mercury must be treated to reduce leachability, while those containing greater than 260 mg/kg of total mercury must be treated to remove mercury prior to disposal in a landfill.

For high-mercury soils, the best demonstrated available technology (BDAT) is specified as thermal roasting or retorting. However, for the situation faced by the natural gas industry, the national capacity to treat soils by the BDAT, is insufficient and may not provide the most cost-effective and efficient remediation methodology. The USEPA,

however, does allow for the development of alternative treatment technologies that can achieve performance-based standards.

3.0 GOALS AND OBJECTIVES

The objective of this research was to identify and evaluate currently available and developing technologies that can be applied to the remediation of mercury-contaminated gas metering sites within the natural gas industry. A request for proposals (RFP) was issued to companies that expressed an interest in developing and demonstrating remediation technologies for the removal of mercury from soils. Nine responses to the RFP were received, but only three different technologies were proposed for demonstration. These included thermal treatment, physical separation, and chemical leaching.

Each of the demonstrations was conducted in compliance with a quality assurance/quality control (QA/QC) plan (Fraley and Stepan, 1993) developed specifically for the project (see Appendix A). The QA/QC Plan with supporting documentation, which was designed to emulate the USEPA's Contaminated Soil and Debris (CSD) plan, was to assure that the development and testing of the remediation technologies adequately fulfilled federal requirements relating to quality.

4.0 MERCURY AS AN ENVIRONMENTAL CONTAMINANT

A successful remediation effort requires a thorough understanding of the physical, chemical, hydrological, mineralogical, and biological processes that affect the transport and fate of mercury at a given site. This understanding will provide the basis for the development and/or selection of effective, economical remediation alternatives.

Mercury exists in both organic and inorganic forms and may occur in three different valence states: as elemental mercury in the Hg^0 state and as ionic mercury in either a Hg^+ or Hg^{2+} state. Elemental mercury, one of few metals that is a liquid at room temperature, has a melting point of −38.87°C (−37.97°F) and a boiling point of 356.6°C (673.9°F). It is 13.5 times more dense than water and approximately 5 times more dense than most soils. It has a vapor pressure of 0.0012 mmHg at 20°C (68°F), which increases rapidly by orders of magnitude with relatively small increases in temperature.

There is a strong tendency for mercury, in all of its elemental, ionic, and organomercurial forms, to sorb to nearly every available surface, including sediments and soil organic matter. The positive aspect of this behavior is that mercury is not highly mobile under most environmental conditions. However, mercury is known to associate with suspended solids and colloidal matter in aquatic systems. Thus mercury attachment and transport on fine particles is a likely candidate as a supportable hypothesis for mercury mobility.

Another important factor to be considered in the transport and fate of elemental mercury from gas industry sites is the particle-size distribution of mercury droplets. Although the mass of mercury at any given site is important in transport considerations, the rate of transport of the metal, directly or through secondary chemical reactions or transformations, will be largely controlled by its total surface area. Thus a site with a

kilogram of mercury in one large puddle may be less problematic than a site with one hundred grams of mercury dispersed in millimeter-sized droplets. The dispersion of mercury in small droplets could result in a more rapid volatilization or oxidation caused by the greater surface area, resulting in an increased transport potential for the mercury and resulting mercuric compounds.

Bacterial and abiotic chemical processes can methylate mercury(II) ions in both waters and geological materials. Many animals and certain plants, such as algae, can readily acquire methylmercury. Compared to elemental mercury, methylmercury is more easily absorbed by fish and other aquatic fauna, either directly through the gills or by ingestion of contaminated aquatic plants and animals (Bogle, 1972). Human exposure may result via three pathways: inhalation, ingestion, and dermal absorption. The most widespread mercury-related health problem among humans involves the consumption of water fauna, such as fish, that have been contaminated with methylmercury. However, the exposure pathway of greatest concern to gas industry workers at meter houses is the inhalation of mercury vapors.

5.0 TECHNOLOGY DEMONSTRATION OVERVIEW

Mercury is a unique contaminant and poses problems that may require innovative remedial solutions. A number of technologies have application for remediation of geologic materials, including physical separation, chemical leaching, thermal treatment, and stabilization and immobilization (Stepan and others, 1993). It is important to note that a single technology may not be adequate to address all the remediation needs of mercury-contaminated sites. Rather, strategies will often be required that combine several technologies for removing the varying forms of mercury under varying environmental conditions at given gas industry sites.

Three technologies or combinations of technologies were selected for demonstration of the removal of mercury from soils, including 1) a pilot-scale, portable thermal treatment system; 2) a pilot-scale physical separation process in conjunction with chemical leaching; and 3) a bench-scale chemical leaching demonstration.

5.1 Soil Characterization

Two different soil types were selected for the treatability demonstrations: a sandy soil collected from gas metering sites in New Mexico and a clayey soil collected from gas metering sites in Ohio. The only known RCRA contaminant in either of the soils was mercury. In order to evaluate and compare the effectiveness of treatment of the individual remediation processes, the excavated soils were mixed and split to provide relatively uniform feed material for the three demonstrations.

Following the splitting and mixing, grab samples of the sandy soil were found to contain approximately 15,000 mg/kg of total mercury, of which over 95 percent was in the elemental form. The sandy soil sample also contained miscellaneous debris, including 1.5-volt batteries, nails, paper, and small twigs. The clayey material contained debris, including small branches, glass, duct tape, roots, styrofoam, and plastic. The total mercury concentration in the clayey soil was found to be approximately 1000 mg/kg, with less than 20 percent in the elemental form.

5.2 Thermal Treatment

5.2.1 Introduction

A patented portable thermal treatment (PTT) process has been designed by Pittsburgh Mineral & Environmental Technology (PMET) Inc., in conjunction with Mercury Recovery Services (MRS), New Brighton, Pennsylvania. The treatment system processes soils contaminated with elemental mercury, mercury compounds, and amalgams while treating the process gas emissions and recovering mercury as a commodity product.

The pilot-scale, mobile treatment unit is a trailer-mounted, electric, two- to three-person operation, able to process a half ton of mercury-contaminated soil per hour. The major components of the pilot-scale unit used for the demonstration include the furnace, condenser, gas-purifying carbon adsorption columns, vacuum pump, valves and piping, and instrumentation for the measurement of soil and gas temperature, gas flow, and the mercury concentration of the gas stream. The complete pilot unit is enclosed by a secondary containment chamber and can be placed onto a truck for mobile field operation. System utilities, including the power transformer, electrical switchgear, and recirculating water chiller are contained in an isolated compartment. The power required to operate this unit is approximately 30 kW.

The process is operated under a negative pressure (slight vacuum) to prevent vapors from escaping into the atmosphere, thus ensuring worker and environmental safety. The process equipment enclosure chamber can also be operated under a slight vacuum, adding redundant safety features to the system. All system and containment chamber gas inlet and exhaust lines have carbon adsorption canisters to treat process gas emissions.

5.2.2 Demonstration

For the demonstration, the PMET/MRS PTT process was conducted in a batch mode. Figure 1 is a process diagram for the PMET/MRS thermal treatment process. Mercury-contaminated soils were mixed, split, and blended with a proprietary additive. The soils and additive were then heated at a low temperature in the furnace to remove soil moisture. After drying, the furnace temperature was increased to volatilize the remaining mercury. The mercury vapors were condensed and the mercury recovered in a collection pot. All gas emissions from the process were passed through sulfur-impregnated activated carbon adsorption columns. No waste streams were produced by this process. The recovered mercury was sent to a refinery for recycling and the spent carbon was regenerated.

5.2.3 Results and Conclusions

Table 1 summarizes the treatability test results for the PMET/MRS PTT remediation process demonstrations. The sandy soils initially contained 12,720 mg/kg total mercury, which was reduced to 0.07 mg/kg following treatment, a 99.999 percent reduction. TCLP mercury was reduced from 0.346 mg/L mercury (above the regulatory limit of 0.2 mg/L) to 0.0005 mg/L. Total mercury in the clayey soil was reduced from 1090 mg/kg to 0.12 mg/kg, a 99.99 percent reduction.

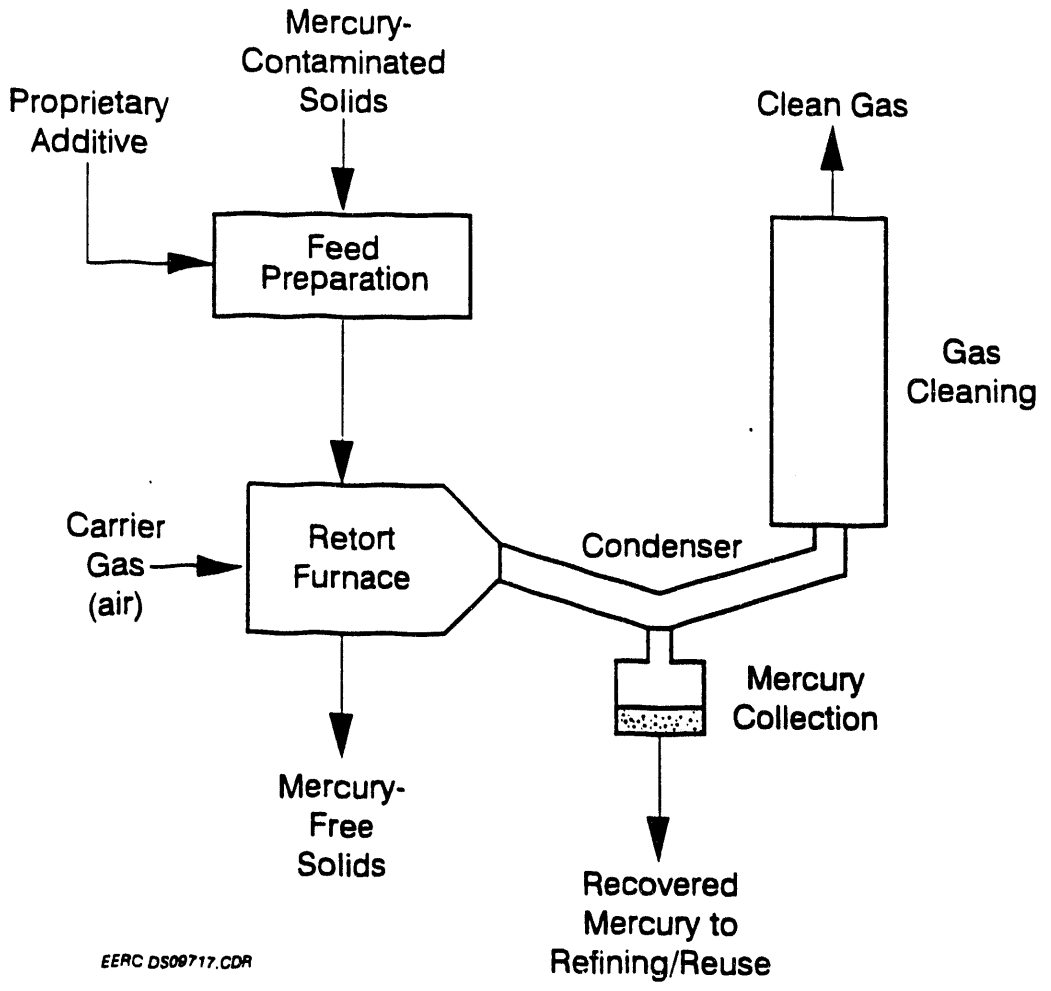

Figure 1. PMET/MRS PTT mercury remediation process diagram.

TABLE 1

Summary of Results of PMET/MRS Mercury Remediation Technology Demonstration

Sandy Soil:	
Initial Sample Weight, kg	68.1
Initial Hg (total), mg/kg	12,720
Final Hg (total), mg/kg	0.07
Initial Hg (TCLP), mg/L	0.346
Final Hg (TCLP), mg/L	0.0005
Clayey Soil:	
Initial Sample Weight, kg	68.1
Initial Hg (total), mg/kg	1090
Final Hg (total), mg/kg	0.12
Initial Hg (TCLP), mg/L	0.065
Final Hg (TCLP), mg/L	0.0008

Based on the data generated during the demonstration, it can be concluded that the PMET/MRS PTT process can remove a variety of mercury forms from a range of soil types. Total mercury was reduced to less than 1 mg/kg and TCLP mercury to less than the current regulatory limit of 0.2 mg/L.

5.3 Physical Separation and Chemical Leaching

5.3.1 Introduction

A pilot-scale physical separation process done in conjunction with a chemical leaching operation has been developed by Mountain States R&D International (MSRDI), Inc., Vail, Arizona. The technology involves physical separation of elemental mercury by conventional gravity concentration, followed by a chemical leaching procedure to extract the remaining complexed metal. The solubilized mercury is chemically precipitated and then retorted, producing elemental mercury.

5.3.2 Demonstration

A diagram of the MSRDI mercury-contaminated soil remediation process is shown in Figure 2. For demonstration purposes, it was operated as a semicontinuous batch process consisting of mixing, screening, gravity separation and concentration, chlorine leaching, and mercury precipitation and recovery.

A weighed amount (approximately 45 kg) of contaminated material was placed in a cement mixer along with water to produce a slurry of relatively uniform consistency. The slurry was then passed through a 10-mesh stainless steel vibrating screen for size

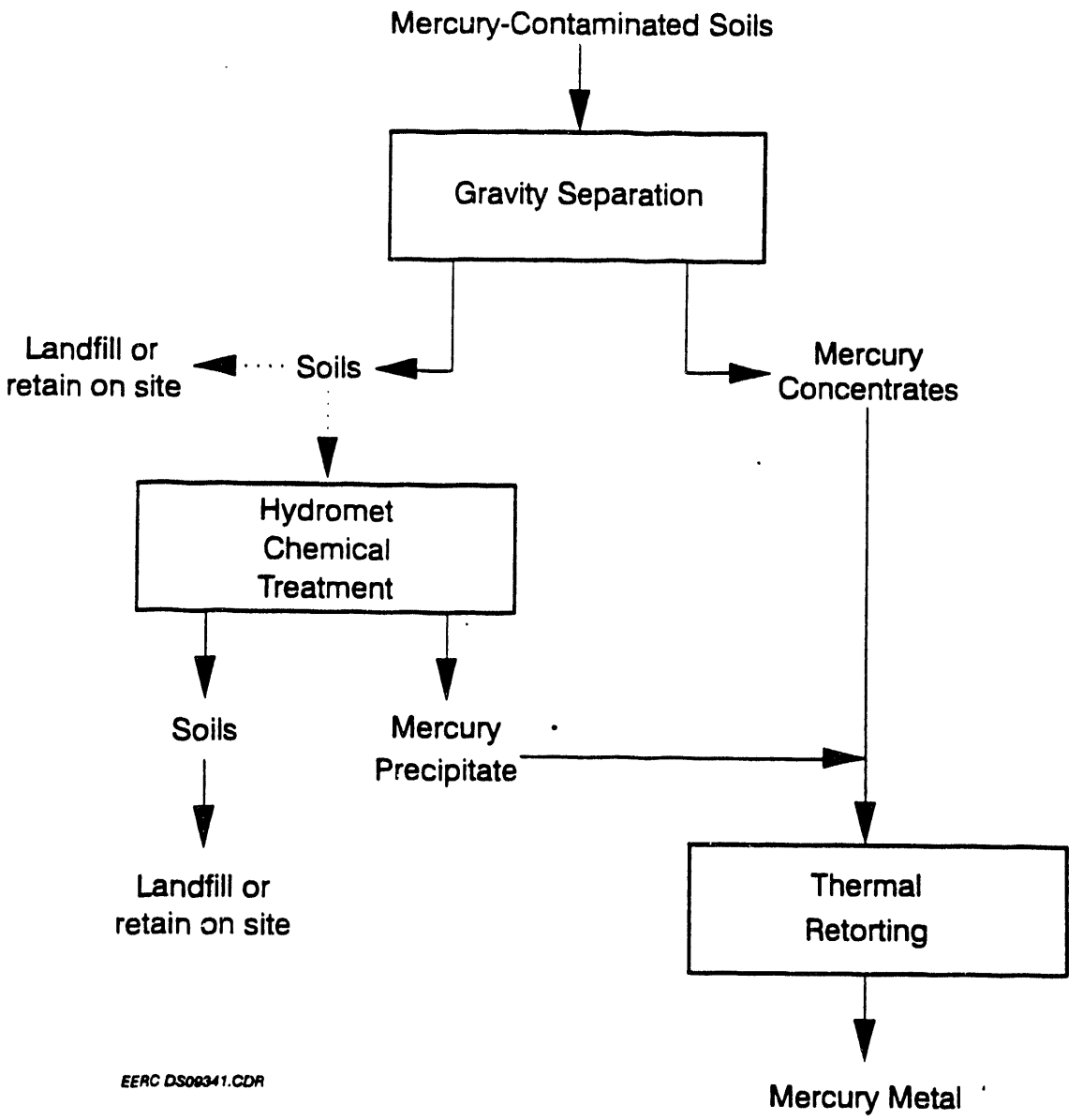

Figure 2. MSRDI mercury remediation process diagram.

separation. Material larger than 10 mesh was collected and analyzed prior to further processing by retorting or disposal.

Material smaller than 10 mesh was pumped to a two-stage Neffco concentrator to separate most of the elemental mercury. The heavy materials, including elemental mercury, were retained in the Neffco concentrators, removed after the batch had been processed, and subjected to further separation using a spiral concentrator. The fine materials were collected in a thickening tank, at which point a flocculating agent was added to promote gravity settling.

Thickened material was transferred to a chlorine leaching vessel. The leaching vessel consisted of a polyethylene tank with a mixer to maintain solids suspension. Chlorine gas, used as a leaching agent, flowed through a diffuser located at the bottom of the tank. Excess chlorine was vented through the top of the tank and discharged to the atmosphere by a blower assembly.

The leached solids were then pumped to a pan filter for rinsing and the removal of excess water. The filtrate (leaching solution) was pumped to a mercury recovery tank, where it was contacted with aluminum powder to precipitate and recover elemental mercury.

5.3.3 Results and Conclusions

A summary of results of the MSRDI demonstration is provided in Table 2. Physical separation resulted in the recovery of 579.8 g of elemental mercury from the sandy soil, corresponding to 1.29 weight percent of the original material. This accounts for a mercury reduction of greater than 84 percent during the physical separation. Chemical leaching of the thickened material reduced total mercury concentrations in the sands to approximately 10 mg/kg.

However, where the mercury is more tightly bound to a clayey soil, physical separation accounted for a recovery of less than 30 percent of the original mercury in the sample. Chemical leaching of the thickened clay materials resulted in a total mercury concentration of approximately 1300 mg/kg. Subsequent leaching trials using calcium hypochlorite as a leachant at a dose of 20 pounds per ton of soil resulted in a total residual mercury concentration of 33 mg/kg.

5.4 Chemical Leaching

5.4.1 Introduction

A bench-scale chemical leaching process was demonstrated by COGNIS, Inc., Santa Rosa, California. The technology uses a leaching–extraction–stripping process to leach mercury from contaminated soil using proprietary aqueous leaching solutions. The leachant is specifically matched to the soil matrix, as well as to the concentration and species of mercury contaminants.

A process diagram for the COGNIS mercury-contaminated soil remediation process is shown in Figure 3. The overall process consists of physical soil washing and particle-size classification, oxidative leaching of mercury from the soil matrices, and removal and

TABLE 2

Summary of Results of MSRDI Mercury Remediation Technology Demonstration

Sandy Soils	
Initial Sample Weight, kg	44.9
Initial Hg (total), mg/kg	15,370
Recovered Elemental Hg, g	579.8
Final Hg (total), mg/kg	10
Clayey Soils	
Initial Sample Weight, kg	44.0
Initial Hg (total), mg/kg	920
Recovered Elemental Hg, g	10.8
Final Hg, total, mg/kg	1300
Final Hg, after releaching, mg/kg	33

recovery of dissolved mercury from the leachate via electrodeposition. The demonstration conducted for this project focused on the oxidative leaching process and the recovery of mercury from the loaded leachant.

5.4.2 Demonstration

Prior to the bench-scale demonstration, both the clayey and sandy soil samples were physically separated into oversize, coarse, and fine-size fractions by Brice Environmental Services Corporation (BESCORP) at their facility in Fairbanks, Alaska. Leaching tests for the demonstration were performed on the coarse and fine-size fractions. There was no attempt to optimize the physical separation for the removal and recovery of elemental mercury prior to leaching.

The primary goal of this demonstration was to reduce the residual total mercury concentrations in the contaminated soil after leaching treatment to below the desired upper limit, 15 mg/kg Hg in soil, and also to have the soil pass the TCLP for mercury. If this was not found to be feasible, the secondary goal was to reduce the residual total mercury concentrations to <260 mg/kg and have the soil pass the TCLP for mercury, allowing disposal of the treated soil in a landfill.

Two soil sample types were treated under the same conditions, with the exception of temperature. Two different proprietary leachants were evaluated during the demonstrations. Leachant A was a halogenated solution contacted with the soils under ambient conditions (room temperature). Leachant B was a nonhalogenated solution contacted with the soils at 50°C.

The leaching tests consisted of placing 4-g samples in 50-mL centrifuge bottles, along with 20 mL of leachant solution. The sample bottles were then capped and agitated for 1 hour. At the end of the 1-hr contact period, the bottles were centrifuged to facilitate

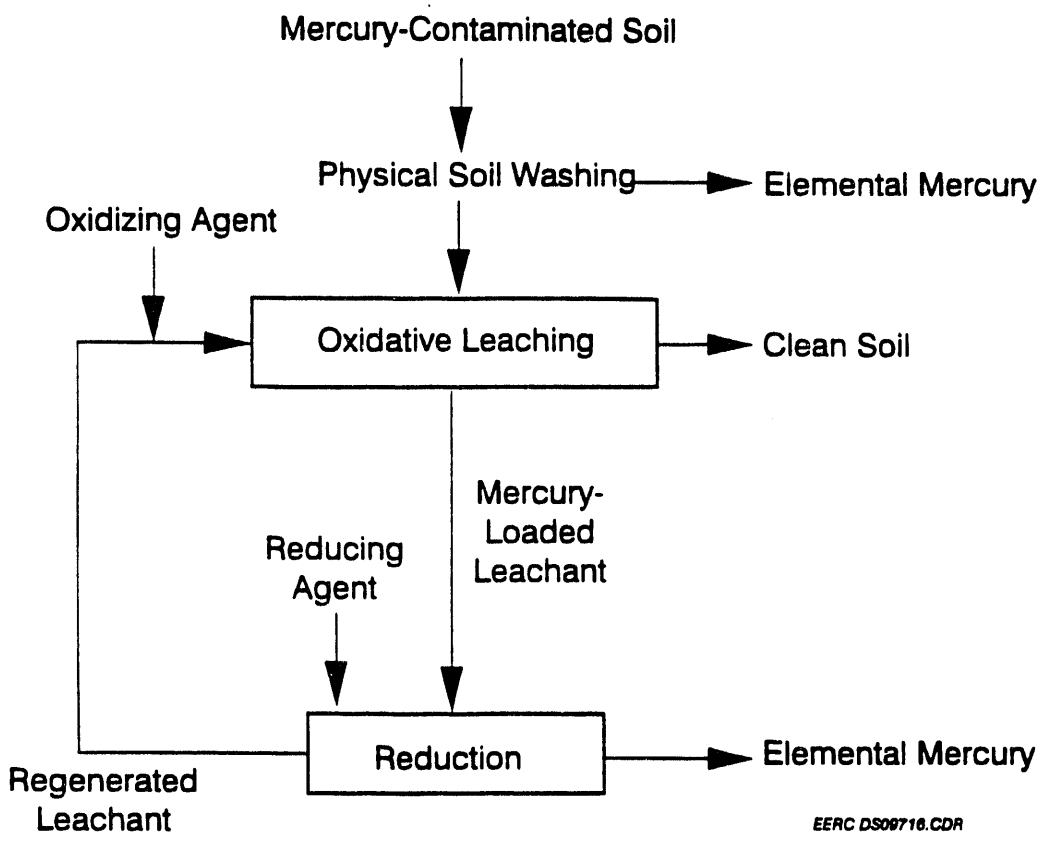

Figure 3. COGNIS mercury remediation process diagram.

solids separation. The leachate was then decanted from the sample and a fresh 20-mL volume of leachant was added to the sample. This procedure was repeated so that each soil sample was subjected to five 1-hr contact periods using fresh leachant for each contact.

5.4.3 Results and Conclusions

Preliminary results of the bench-scale leaching tests using Leachants A and B are summarized in Table 3. Leachant A showed greater removal efficiency over Leachant B during the demonstration. Residual mercury in the treated sandy soil was reduced to less than 5 mg/kg, well below the target level of 15 mg/kg, using Leachant A. Most of the mercury (greater than 98 percent) was removed from the sandy soil after three contact periods.

The fine and coarse fractions of the clayey soil were leached to approximately 15 mg/kg and 38 mg/kg, respectively, after five contacts using Leachant A. These results meet the secondary goal of 260 mg/kg residual total mercury. The clayey soil was found to be more difficult to leach because of the higher content of organic material. The organic material tends to bind metals tightly and also consumes considerable oxidant. These results indicate that more leaching contacts, or longer contact times, will be required to reduce the residual mercury in the clayey soil to less than 15 mg/kg.

TABLE 3

Summary of Results of COGNIS, Inc., Mercury Remediation Technology Demonstration

	Leachant A	Leachant B
Sandy Soil		
Fine-Size Fraction		
Initial Hg (total), mg/kg	848	738
Final Hg (total), mg/kg	2.8	30
Coarse Fraction		
Initial Hg (total), mg/kg	2130	2220
Final Hg (total), mg/kg	4.2	72
Clayey Soil		
Fine-Size Fraction		
Initial Hg (total), mg/kg	865	861
Final Hg (total), mg/kg	15	127
Coarse Fraction		
Initial Hg (total), mg/kg	1040	1080
Final Hg (total), mg/kg	38	119

6.0 SUMMARY

Three different technologies, or combinations of technologies, were evaluated for their ability to reduce mercury concentrations in two different soil types having distinctly different contamination scenarios. Preliminary results indicate that portable thermal treatment and physical separation processes used in conjunction with chemical leaching may be effective remediation alternatives to commercial thermal treatment. Ultimately, developing the most effective mercury remediation strategy for use at gas metering stations will depend on several factors (Stepan and others, 1993):

- Predominant form in which the mercury exists
- Type of contaminated soils and the presence of other contaminants and debris
- Distribution of mercury within the contaminated materials
- Level to which the contaminated site must be remediated

7.0 REFERENCES

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APPENDIX A
QUALITY ASSURANCE/QUALITY CONTROL PROJECT PLAN

THE DEVELOPMENT AND TESTING OF TECHNOLOGIES FOR THE REMEDIATION OF MERCURY-CONTAMINATED SOILS

Quality Assurance/Quality Control Project Plan

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THE DEVELOPMENT AND TESTING OF TECHNOLOGIES FOR THE REMEDIATION OF MERCURY-CONTAMINATED SOILS

1.0 INTRODUCTION

This Quality Assurance/Quality Control (QA/QC) Project Plan defines the requirements and the organizational responsibilities for each major section of the project entitled "The Development and Testing of Technologies for the Remediation of Mercury-Contaminated Soils." This plan also includes the supporting documents required for a comprehensive QA/QC project.

Compliance with this QA/QC project and its supporting documents will assure that the development and testing of the remediation technologies adequately fulfill federal and state requirements relating to quality. The QA/QC team leader is responsible for resolving any conflicts relative to complying with the requirements of this project.

The operation and schedule of this project will emulate that of the Environmental Protection Agency's (EPA) Contaminated Soil and Debris (CSD) plan. Figure 1 presents an example of a schedule for the tasks involved in the mercury technology demonstration project. It will serve as a template to follow for completing the QA/QC project plan.

2.0 PROJECT DESCRIPTION

The purpose of this project is to investigate a range of remediation technologies for mercury-contaminated soils at gas metering sites. The goal of this investigation is to establish criteria and parameters for the available remediation options, to allow the industry to deal with each unique situation in the most efficient, cost-effective, and environmentally sound manner.

The remediation technologies of three companies will be investigated: 1) Pittsburgh Mineral and Environmental Technology, Inc.'s (PMET) mobile thermal retorting system; 2) COGNIS, Inc.'s oxidative leaching process; and 3) Mountain States R&D International, Inc.'s (MSRDI) physical separation (gravimetric) process, followed by leaching.

The Energy & Environmental Research Center (EERC) will oversee the three subcontracted projects to maintain consistency in the data collected and to validate the results of each project by witnessing the demonstration tests and performing duplicate sampling and analysis during the tests. Duplicate samples of waste streams, process waters, and cleaned soils will be analyzed at the EERC laboratories.

3.0 PROJECT ORGANIZATION AND RESPONSIBILITY

The QA/QC control functions have been organized to allow independent review of project activities. The objective of the QA/QC efforts is to assess and document the precision, accuracy, and adequacy of the data derived from the investigation. Figure 2 shows project authority lines.

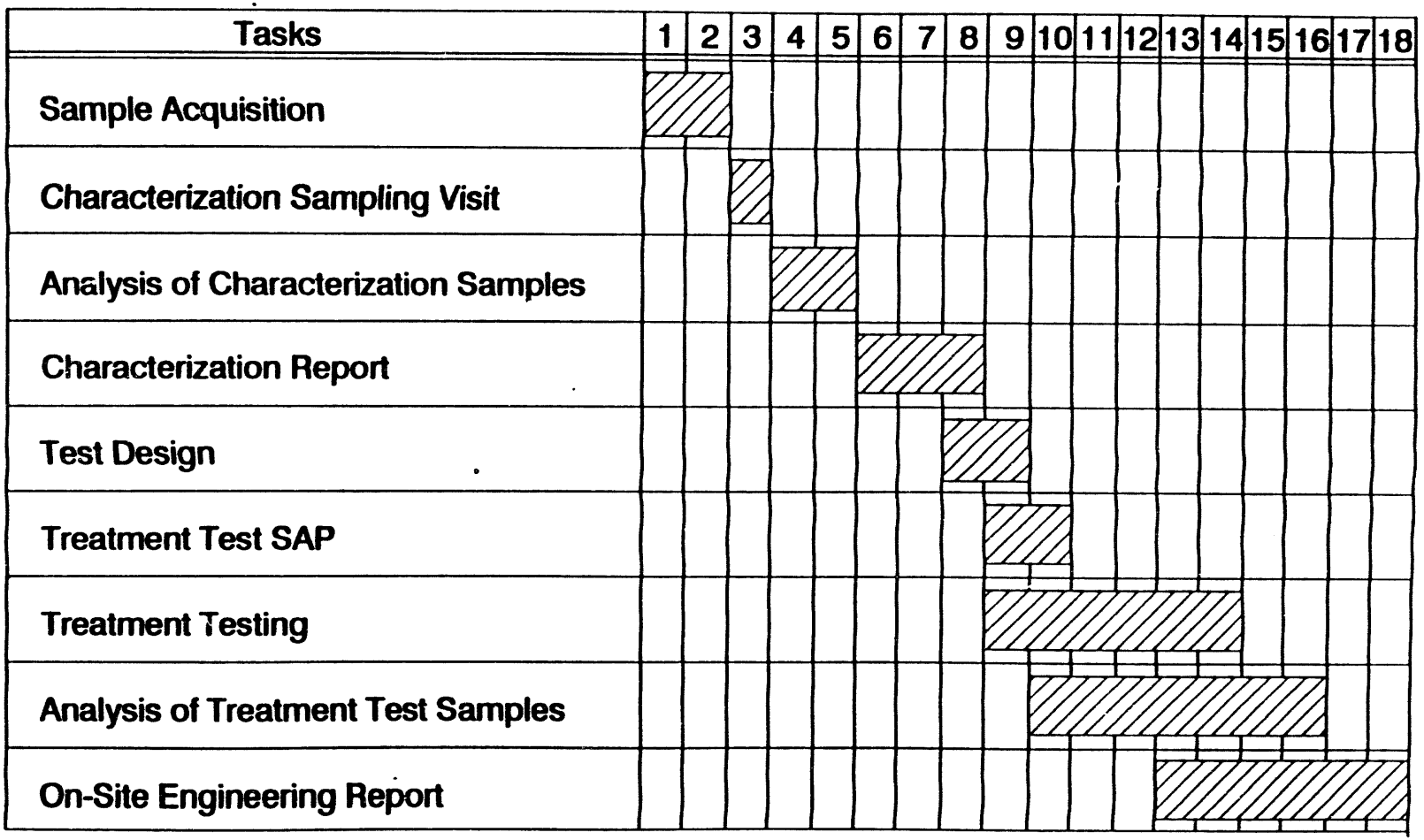

Figure 1. General schedule for mercury remediation technology demonstration project data collection efforts.

The mercury technology demonstration investigation is managed by a task force composed of the following key personnel from the EERC:

- Project Directors: Frank Beaver and Craig Schmit
- Project Manager: David Charlton
- QA/QC Team Leader: Rose Fraley
- Research Manager: Dan Stepan
- Analytical Team Leader: Dave Hassett
- Health and Safety Officer: Ken Grohs

3.1 Project Directors

The project directors function as a board of directors to establish the overall policy and direction of the project. They assign personnel to the other lead positions in the project organization and generally direct and oversee its operation.

3.2 Project Manager

The project manager is responsible for all functions of the project, including the establishment of QA/QC policies and the delegation of authority to carry out these policies. The project manager is responsible for compliance with the requirements of this manual and will coordinate conflict resolution with the appropriate personnel.

Other duties include, but are not limited to:

- Assigning duties to the project staff.
- Reviewing major project deliverables for technical accuracy and completeness.
- Reviewing subcontractor work and approving invoices.
- Establishing a record-keeping system in conjunction with QA/QC team leaders.
- Controlling the budget and schedule.
- Directing project closeout.

3.3 QA/QC Team Leader

Responsibilities of the QA/QC team leader include:

- Generation and promulgation of the QA/QC project plan.
- Scheduling, planning, and conducting quality audits; issuing audit reports; retaining audit records; and following up on corrective actions.

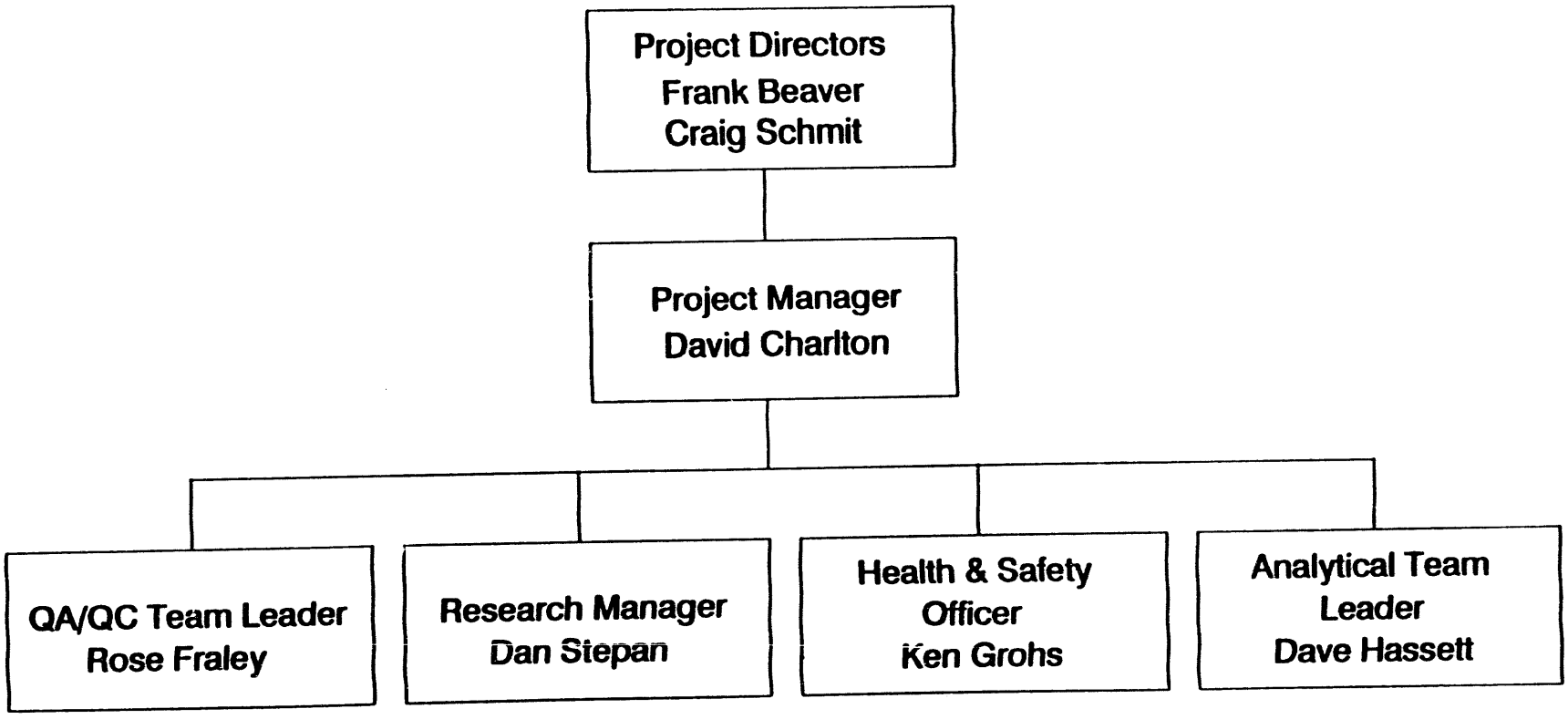

Figure 2. Task force organizational chart.

3.4 Research Manager

The research manager is responsible for ensuring that data are collected, analyzed, reported, and stored in a manner consistent with the quality policy. The research manager will also provide technical and scientific support to the project manager and other work groups for the quality-related aspects of the investigation. Other duties will include:

- Designing the field investigation, including sampling locations.
- Supervising field personnel who monitor demonstration progress and perform sample collection and measurements.
- Reviewing all field activities for proper documentation.
- Monitoring the sampling operations to verify that the subcontractor and sampling team members adhere to this QA/QC project plan.
- Maintaining the central filing system.
- Coordinating activities with the project manager.

3.5 Health and Safety Officer

The health and safety officer is responsible for leading all health and safety program efforts in accordance with appropriate Occupational Safety and Health Administration (OSHA), EPA, and EERC standards. Other duties will include:

- Issuing project-specific health and safety plans addressing such topics as medical surveillance, training, workplace exposure monitoring, personal protective equipment, and emergency response.
- Training, assigning, and supervising other site health and safety officers.
- Conducting on-site health and safety audits.
- Coordinating implementation of associated corrective actions.
- Halting site activities if health and safety practices are inadequate.
- Participating in reviews to ensure that safety is integrated into those phases.

3.6 Analytical Coordinator

Responsibilities of the analytical coordinator include:

- Establishing sampling and testing programs in conjunction with the project manager and the QA/QC team leader.

- Reporting of nonconformances and changes in laboratory activities.

- Serving as a liaison between the project and laboratory personnel, notifying both groups of specific lab nonconformances and changes.

- Reviewing and releasing analytical results.

4.0 QA/QC DATA QUALITY OBJECTIVES

It is the objective of this QA/QC project plan to ensure the quality of field and laboratory data so that all measurements yield results representative of the media (air, water, solids, etc.) and conditions being measured. The plan will also ensure that all data are calculated and reported in units consistent with other organizations, to allow for comparability.

Data collected in this manner will satisfy the overall objective for the remediation program's sampling and analysis efforts: to produce well-documented, quality data that can be used to determine the best demonstrated available technologies (BDAT) for various mercury-contaminated soils and to develop BDAT treatment standards for those soils. The types of data that will be produced fall into two categories: characterization data and treatment data.

Characterization data, e.g., data from soil samples collected before treatment, provide information on contaminant concentrations and other physical/chemical characteristics that may affect the performance of the technology selected for evaluation.

Treatment data, e.g., data resulting from treatment tests, provide information on untreated soils and treatment residuals, as well as design and operating information concerning the treatment system. Treatment data will be used to evaluate the remediation ability of the technology.

The quality of the analytical data for this project will be measured by the following data quality indicators: analytical method detection limits, precision, accuracy, completeness, representativeness, and comparability. These indicators will ensure that all information, data, and resulting decisions are technically sound, statistically valid, and properly documented.

4.1 Detection Limits

Matrix detection limits are to be calculated for the untreated soils and each residual sample following the test methods given in SW-846 (Test Methods for Evaluating Solid Waste, SW-846, 1986), where applicable. For diluted samples, the matrix detection limit will be calculated as the detection limit for the particular matrix multiplied by the dilution factor.

The matrix detection limit should be calculated following the procedures described in Section 1 of SW-846. The method detection limit is calculated by multiplying the standard deviation, calculated from three replicates, by 6.9.

4.2 Precision and Accuracy

Precision is defined in terms of relative percent difference of the matrix spike and the spike duplicate, where applicable. Precision is calculated using the following equation:

$$RPD(\%) = \frac{(C_1 - C_2)}{(\frac{C_1 + C_2}{2})} \times 100 \qquad \text{[Eq. 1]}$$

where RPD = relative percent difference, C_1 = the larger of the two values, and C_2 = the smaller of the two values.

Accuracy is defined in terms of percent recovery of laboratory matrix spikes. For untreated soil samples, a matrix spike for mercury will be conducted. For the treatment test analysis, a matrix spike and a spike duplicate will be completed on one sample of the untreated soil and one sample of each treatment residual. If treatment test samples are highly concentrated (greater than 1%), duplicate analyses may be substituted for the matrix spike duplicate analyses.

Accuracy is calculated using the following equation for percent recovery:

$$\%R = \frac{o_i - o_s}{T_i} \times 100\% \qquad \text{[Eq. 2]}$$

where %R = percent recovery, o_i = observed spike sample concentration (mg/L), o_s = sample concentration (mg/L), and T_i = true concentration of the spike (mg/L).

$$T_i = \frac{C_i \times V_i}{V_s + V_i} \qquad \text{[Eq. 3]}$$

where C_i = concentration of spike (mg/L), V_i = volume of spike (mL), and V_s = volume of sample (mL).

The spike constituents will be determined on an individual basis and will be presented in the technology-specific sampling and analysis plan (SAP). Spiking will be completed at the laboratory prior to extraction or digestion. The spike concentrations must either be 50 to 150 percent of the initial concentration level prior to spiking, or 10 times the expected matrix detection limit if the constituents are expected to be at the nondetect level.

Recoveries for the matrix spike and spike duplicate should be at least 20 percent. If recoveries are less than 20 percent or greater than 200 percent, the data must be reviewed.

4.3 Completeness

Completeness is defined as the number of initiated activities that are actually finished. For this project, the activity begins with acquiring the samples while observing the demonstrations and ends with reporting the results. The degree of completeness is the number of samples for which acceptable analytical data are generated divided by the total number of samples collected multiplied by 100. The QA/QC objective for completeness in the sampling and analyses efforts is 100 percent. If the completeness is less than 100%, documentation will be required to explain why the QA/QC objective was not met and to describe the effect on the project.

4.4 Representativeness

Representativeness is addressed through selection of appropriate sampling locations and procedures. The goal for the treatment tests is to obtain samples representative of the untreated matrix and treatment residuals such that the performance of the treatment can be evaluated. This can be accomplished by obtaining matched in and out sample pairs (or sets) of the untreated matrix and treatment residuals, accounting for residence times. Treatment test samples should be composites of three subsamples unless grab samples adequately represent the matrix being analyzed. Debris and foreign objects will be removed from the soil samples, if possible.

4.5 Comparability

For this project, comparability for each treatment test will be addressed through use of identical analytical procedures. The analytical data will be reported in the same units for each test for all samples collected during each treatment test.

5.0 COLLECTION PLAN FOR SAMPLES

Two different soil types will be shipped to MSRDI for mixing and splitting. The two soil types are intended to represent some level of the variability of mercury-contaminated soils at gas industry sites.

Five 55-gallon drums of clayey soil will be shipped from Ohio, and three 55-gallon drums of sandy soil will be shipped from New Mexico. Once all drums are received, MSRDI will be responsible, under the supervision of an EERC representative, for mixing and splitting the soils and distributing the samples to the three subcontractors.

The sampling and collection plan will be unique for each of the three subcontractors. These plans are outlined in greater detail in the technology-specific SAP and on-site engineering report (OER) and include the following:

- Sampling point descriptions
- Sampling collection method
- Sampling schedule
- Constituent(s) to be analyzed
- Total composition and toxicity characteristics leaching procedure (TCLP) extracts
- Sample containerization and preservation
- Design and operating data collection

5.1 Sampling Procedures for Characterization Samples

The criteria used to determine the number of samples and the sampling points for each demonstration are detailed in each technology-specific SAP. The procedures used to collect the samples will vary depending on the location of the sample point in the process. The SAP also includes a description of the equipment that will be used to collect the samples and documentation on how the samples are to be collected and composited. The final characterization report will document the location of the samples and any deviations or modifications from the SAP that were required to take samples.

5.2 Sampling Procedures for Treatment Tests

The soil may require some preparation prior to being treated, e.g., grinding or blending. The SAP discusses which procedures to use and the OER documents the exact procedures that were used. The untreated samples for the test must be collected after the preparation step.

The SAP also describes sampling procedures, locations, and frequencies. Sampling times for the untreated and treated samples must account for the residence time of the treatment system. The untreated and treated samples must be corresponding, matched pairs, to allow for the evaluation of waste characteristics and completion of a material balance around the unit. Any deviation from obtaining matched pairs must be documented in the SAP and must be approved by the project manager. It is suggested that six sets of untreated and treated samples be collected. However, the final decision regarding the number of sampling sets needed to evaluate the treatment system must be approved by the project manager and described in the treatment test SAP.

All samples collected during the treatment tests will be a composite of three subsamples, unless grab samples are determined to adequately represent the matrix being evaluated. All debris must be removed from the untreated soil subsamples. The subsamples must be broken up and mixed/blended prior to compositing. The sample aliquots for each analytical test will then be taken from the composited material. The technology-specific SAP must document the manner in which the subsamples are to be collected and composited. The OER must document the location from which the subsamples were taken and any deviations or modifications from the SAP that were required to take the samples.

A matrix spike and a spike duplicate analysis must be completed for the untreated soils and the treatment residual. These spikes will be prepared in the laboratory. The sample set and the constituents to be spiked, along with the concentration level of the spike constituents, must be specified in the SAP.

Design and operating data must be collected in addition to samples for analysis. The SAP must specify the design and operating data to be collected, their importance, and where, how, and how frequently they are to be collected.

5.3 Field QA/QC Activities

5.3.1 Representativeness

Sampling locations will be chosen so that they are representative of the untreated soil and the treatment residuals obtained from the treatment system under investigation. The sample volume to be collected must be sufficient for analytical tests. Debris will be removed from all samples prior to treating. The subsamples from field composite samples will be mixed thoroughly before sending the sample aliquots to the laboratory.

5.3.2 Backup Samples

A backup sample aliquot will be taken to ensure the 100 percent completeness data QA/QC objective. If backup samples are collected, they must be shipped in separate packages to ensure that a complete set of samples arrives at the laboratory. The chain-of-custody forms will identify the backup sample aliquots, which will be labeled "hold for analysis", and will be analyzed only if the original sample is damaged or lost in shipment.

5.3.. Containers

All sample containers will be cleaned prior to use following USEPA protocols specified in SW-846 (Test Methods for Evaluating Solid Waste, SW-846, 1986). The sample containers may be cleaned in the laboratory or may be purchased precleaned.

5.3.4 Blanks

Blank samples, i.e., equipment blanks, trip blanks, and field blanks, will be collected during characterization sampling visits and treatment tests. All blanks from treatment tests must be analyzed as specified in the individual treatment test SAPs. Analysis of blanks collected during the characterization sampling visits is not a requirement, although it may be warranted in cases where contamination is suspected.

Equipment blanks. Equipment blanks are used to determine if glassware and other field equipment are a source of contamination. An equipment blank will be collected if field equipment is to be decontaminated and reused. One equipment blank per sampling event for a treatment test must be collected and analyzed even if all field equipment is new. If field decontamination procedures are used, they must be documented in the SAP.

Trip blanks. Trip blanks are used to determine if any contamination resulted from sample transport, shipping, or site conditions. One trip blank that is not opened in the field will be taken. The trip blank will be prepared by pouring laboratory pure water into a sample container, which will be packed and shipped with the sample containers throughout the entire process. (Laboratory pure water, as defined in SW-846, is distilled or deionized water or Type II reagent water that is free of contaminants that may interfere with analysis.)

Field Blanks. Field blanks are collected to verify that contamination from volatile material has not occurred. Each field blank will consist of laboratory pure water taken to the field and poured into a sample container in the area where the treatment system is located. Field blanks

may be collected based on technology-specific conditions. A field blank for metals may be taken if metal dust and potential atmospheric deposition of the dust are problems at the location and may be a potential source of contamination, especially in the treated residuals.

If constituents of interest are measured in the blank, documentation will be presented in the OER that explains the impact of the contamination on the samples collected.

5.4 Sample Preservation and Containerization

All samples will be preserved in the field. The SAP specifies the containers, sample size, holding times, and sample preservation requirements for each analytical parameter for every sample matrix. The laboratory will be contacted to determine the sample volume required to complete each analysis. The containers will be filled to the top to ensure that a sufficient amount of sample is available for the analysis. Table 1 provides the information concerning the containers, sample sizes, holding times, and sample preservation requirements for various analytical parameters used in mercury analyses. Teflon™ is preferred for water samples.

TABLE 1

Sample Containers, Sizes, Holding Times, and Preservation Requirements for Mercury Samples

Parameter	Container	Sample Size	Holding Time	Preservation
Wastewaters				
Total Metals	P, G	1-L jar	28 days	2% BrCl cool ≤4°C
TCLP (metals only mercury)	P, G, T	1-L jar	28 days to extraction and analysis	2% BrCl cool ≤4°C
Soils and Sediments				
Total Metals/ TCLP (metals only mercury)	P, G, T	One 500-mL wide-mouth jar	28 days to extraction and analysis	cool ≤4°C
Sludges				
Total Metals/ TCLP (metals only mercury)	P, G, T	Two 1-liter wide-mouth jars	28 days	cool ≤4°C

P = plastic, G = glass, T = Teflon™

5.5 Split Sampling

If split samples are to be taken at the time of sample collection, the following procedure for providing split samples should be used:

1. At the time of sample collection, a sufficient amount of sample for both the site and the laboratory sample is taken. For samples to be composited, the subsamples are taken as grabs. The debris is removed, and the samples are then homogenized, composited, and split. The aliquots are then transferred to the appropriate sample containers. For grab samples, sufficient sample is taken, mixed, and transferred to the appropriate sample containers.

2. Observations and judgments about sample homogeneity and the fact that split samples were provided are recorded in the field logbook.

5.6 Sample Collection

Technology-specific SAPs will be developed for each characterization and treatment test sampling visit. The technology-specific SAPs contain sample collection protocols that address the following considerations:

- *Sampling Point Descriptions*. The sampling points selected and the justification for their selection must be described. Sampling points will be identified on the schematic diagram for the treatment system.

- *Sample Collection Method*. Sample collection procedures must be described for each sample location. All samples will be composites unless it has been determined that grab samples will adequately represent the matrix. For the characterization sample, the composite will be composed of six subsamples. For the treatment test, composite samples of the untreated soil and treatment residuals will be composed of three subsamples.

- *Frequency*. The frequency of sample collection at each sampling location will be specified in the SAP and selected to best characterize the variability in 1) the soil sample, 2) the treatment process, and 3) the analytical results. If possible, for the treatment test, six sets of untreated and treated samples will be collected. Sampling times for the untreated and treated samples must take into account residence times of the treatment system. The untreated and treated samples are to be corresponding matched pairs.

- *Constituents to be Analyzed*. All analyses will be performed using SW-846 or other EPA-approved methods.

- *Total Composition and TCLP Extracts*. All samples will be analyzed for total composition of CSD list constituents. All nonwastewater treatment residuals, as well as untreated soil samples from stabilization treatment tests, will also be subjected to the TCLP extractions, and the extract will be analyzed for metals.

- *Sample Containerization and Preservation.* Procedures for sample containerization and preservation will be documented in the technology-specific SAPs. A sufficient amount of sample will be collected to complete each requested analysis. In addition, for the sample set for which a matrix spike and a spike duplicate are to be analyzed, a sufficient amount of sample must also be collected for these additional analyses.

- *Quality Control/Quality Assurance.* The number of equipment, trip, and field blanks to be collected and the parameters for which they are to be analyzed are specified in the SAP. In addition to the sample collection considerations, the SAP contains a number of other elements concerning QA/QC protocols.

5.7 Health and Safety Plan

The sampling team will follow health and safety protocols established for each technology-specific demonstration. The health and safety plan will be included as part of the SAP and will document the safety equipment required, the types of chemicals or contaminants that may be present in the samples and/or at the sites, health effects of the contaminants, any special precautions that may be required at the site, the location of the nearest medical facility, and the applicable emergency response phone numbers.

6.0 SAMPLE CUSTODY AND TRANSPORT

6.1 Field Custody

Sample custody will begin, in all cases, at the time of sample collection by placing the sample in an ice chest, or other appropriate container, in the possession of the designated field sample custodian. A line item on the chain-of-custody record form (Figure 3) will be immediately filled out and signed by the field sample custodian. The following information will be included when the chain-of-custody record is filled out:

Project Number	Enter the complete project number.
Project Name	Enter the project name.
Samplers	Enter signature and print name of person or persons who participated in the collection of the samples listed and who should be contacted if questions arise during sample log-in. If the field sample custodian is not listed as a sampler, receipt of documentation is to be indicated.
Field Sample No.	Enter the assigned sample numbers for each sample collected.
Date	Enter date of sample collection. If sample is a composite, indicate both start and finish date.

Time	Enter time of actual sample collection. If sample is a composite, indicate both start and finish time.
Composite/Grab	Indicate by a check the type of sample.
Sample Location	Enter a description of location as well as any location code that has been assigned.
No. of Containers	Enter the number of containers to be shipped for a sample and its replicates.
Parameters	Indicate parameters to be analyzed; if abbreviations or parameter categories are used, further details on exactly what constituents are to be analyzed must be given to the laboratory performing the analysis.
Remarks	Indicate special considerations for a sample (i.e., preservatives used or whether sar ples are to be held pending approval prior to analysis).

Upon completion of all line items, or upon sample pickup, the custodian will sign, date, enter the time, and confirm completeness of all information written on the chain-of-custody record. Each individual who subsequently assumes responsibility for the sample will sign the chain-of-custody record and indicate the reason for assuming custody. The field chain-of-custody records will be completed upon laboratory receipt of samples.

6.2 Sample Transport

Samples prepared for shipment will be packaged and labeled in compliance with current U.S. Department of Transportation (DOT) and International Air Transport Association (IATA) dangerous goods regulations. Any additional requirements stipulated by the overnight carrier will be followed. The packaging and labeling requirements are provided in the technology-specific SAP.

Only a metal or plastic ice chest will be used as the outside shipping container for samples, unless otherwise specified by the shipping regulations. The outside container must be able to withstand a 4-foot drop on solid concrete in the position most likely to cause damage. Each ice chest will be lined with a 6-mil-thick plastic bag. When sample containers are placed in an ice chest for shipment, all samples from a single sampling location, except for duplicate samples, will be kept together as a set unless the SAP specifies otherwise. Duplicate samples will be packaged and shipped in a separate ice chest. Duplicate samples should be marked "hold for analysis" since they are collected only to ensure that a sufficient sample quantity is available should a problem occur during sample transport. Styrofoam or bubble wrap will be used to absorb shock. When more than one set can fit into an ice chest, each of the sets will be placed in separate plastic bags to prevent cross-contamination if breakage occurs.

CHAIN OF CUSTODY RECORD

PROJ. NO.	Project Name/Site Name					Type and No. of Sample Containers	PRESERVATION TECHNIQUE	Requested Analysis				Remarks
SAMPLERS: (Signature)			DATE:									
Sample No.	Date	Time	Comp.	Gras.	Sample Source and Description							

Relinquished by:(Signature)	Date	Time	Received by:(Signature)	Relinquished by:(Signature)	Date	Time	Received by:(Signature)
Relinquished by:(Signature)	Date	Time	Received by:(Signature)	Relinquished by:(Signature)	Date	Time	Received by:(Signature)
Relinquished by:(Signature)	Date	Time	Received for Laboratory by: (Signature)	Date	Time	Remarks:	

Carrier Co: Air Bill No:	Carrier Phone No.	Date Results Reported/by: (Signature)

Figure 3. Example of chain-of-custody record.

After sample containers are sufficiently packaged, the 6-mil-thick plastic bag will be sealed around the samples by twisting the top and securely taping the bag closed to prevent leakage. When preservation requirements dictate, ice will be placed in the chest.

Chain-of-custody records and any other shipping/sample documentation accompanying the shipment will be enclosed in a waterproof plastic bag and taped to the underside of the ice chest lid.

Each ice chest prepared for shipment will be securely taped shut. This can be accomplished with reinforced or other suitable tape (i.e., strapping tape) wrapped at least twice around the ice chest near each end where the hinges are located. A label, or a business card, identifying the name and address of the responsible party will be affixed on the top of each ice chest prepared for shipment.

Sample shipping containers will be marked in accordance with DOT Regulations for Shipping Hazardous Materials (49 CFR 172) and/or IATA Dangerous Goods Regulations, 28th Edition, January 1, 1987. In addition to the complete mailing address, each ice chest must be clearly marked with "this end up" arrows on all four sides.

When sample shipment modes are selected, care will be taken not to exceed allowable holding times for individual samples. All samples will be either delivered by the sampling crew or shipped "Priority One/Overnight" via a commercial carrier. If commercial carriers are used, the proper forms will be completed and attached to the exterior lids of the containers. Multiple shipment forms will be used when shipping more than one container.

If a commercial carrier is used, the sampling crew chief is to supply the following information to the laboratory coordinator: the date on which the samples were shipped, the name of the commercial carrier, the carrier invoice number, the number of shipping containers shipped, and the expected date of arrival at the laboratory.

6.3 Laboratory Sample Custody

Samples will arrive at the laboratory either by delivery by the sampling crew or a courier service. After the ice chests are checked for damage, the samples will be unpacked and the information on the accompanying chain-of-custody records will be examined. If the samples shipped match those described on the chain-of-custody record, the laboratory sample custodian will sign the form and assume responsibility for the samples. If problems are noted with the sample shipment, the laboratory custodian will sign the form, record the problems in the "Remarks" box, and notify the project manager. The laboratory must have a standard operating procedure (SOP) for the laboratory sample custody (Appendix A). The SOP is to include provisions for the laboratory sample custodian.

Any missing samples, broken sample bottles, or unpreserved samples will be noted on the chain-of-custody record. If there are problems with any individual samples, the custodian will inform the laboratory coordinator. The laboratory coordinator will then contact the project manager to determine a solution to the problem.

All samples will then be logged into a sample logbook. The following information will be documented in the logbook:

- Date and time of sample receipt
- Project number
- Field sample number
- Laboratory sample number (assigned during log-in procedure)
- Sample matrix
- Sample parameters
- Storage location
- Log in person's initials

All information relevant to the samples will be secured at the end of each business day. All samples will be stored in a designated sample storage refrigerator/freezer, access to which will be limited to laboratory employees.

7.0 ANALYTICAL PROCEDURES

Analytical methods will be selected from EPA/OSW-approved methods, most of which appear in "Test Methods for Evaluating Solid Waste"(1986). Exceptions to the requirement will be allowed for cases in which the EPA/OSW-approved methods are not appropriate for the preparation or analysis of a specific sample matrix or are not available for a particular constituent or parameter.

Analyses performed by the EERC are presented in Appendix A. These methods are those specified by the EPA and other federal and state agencies and professional organizations, as provided in the following references:

- Guidelines establishing test procedures for the analysis of pollutants under the Clean Water Act, 40 CFR Code of Federal Regulations (CFR), part 136.

- Hazardous waste management, 40 CFR, parts 260-265, 268, and 280.

- EPA, Test methods for evaluating solid waste (SW-846), 2nd ed. (revised), Update I (1984), Update II (1985), 3rd ed. (1986), Office of Solid Waste and Emergency Response.

- APHA, AWWA, and WPC, 1985, Standard methods for the examination of water and wastewater (SM), 16th ed., Washington, DC.

- EPA, Contract Laboratory Program (CLP) protocols for the analysis of organic and inorganic hazardous substances.

- American Society for Testing and Materials (ASTM), Annual book of ASTM standards, V. 11.01, 11.02, and 11.04, ASTM, Philadelphia, Pennsylvania.

Each method used routinely is documented in the form of an SOP. The SOP contains detailed instructions concerning the application of the method. Any deviation from published methodology must be documented and explained in the SOP.

Before a method is routinely used to generate analytical data, the method must be validated by providing the following information:

- Documentation of the method in an SOP, including a summary, detailed description of the analytical procedure, calculations, reporting formats, safety requirements, and special concerns.
- Testing of the method to verify detection limits, linear range, precision, and accuracy.
- Establishment of data acceptance criteria.

Table 2 presents recommended SW-846 methods and other methods for parameters that may be analyzed for in CSD characterization and treatment test samples. All SAPs must specify the exact analytical methods to be employed.

The laboratory must provide documentation concerning the analytical methods used for the constituent parameter of interest and any modifications or deviations required to analyze the various samples, whether an EPA-approved or other method is used. The methods used will be documented in all characterization reports and OERs.

The EERC's Analytical Research Laboratory (ARL) will perform water quality, soil, and waste analyses for the demonstration projects. The EERC uses many of the EPA guidelines as standard operating procedures (Appendix A).

8.0 QA/QC PROCEDURES

The overall efficacy of a QA/QC project depends on operating in accordance with a program that ensures the precision and accuracy of analyses by detecting and identifying errors and preventing their recurrence, or measuring the degree of error inherent in the methods applied.

Most of the analytical methods to be used give guidelines for number and frequency of replicates, matrix spikes, and calibration standards. The matrix spikes, replicates, calibration standards, etc., are analyzed the same way as the field samples. The analytical results are used to document the validity and control of data.

9.0 QA/QC PERFORMANCE AND SYSTEM AUDITS

This section describes procedures and responsibilities for conducting quality audits, accomplishing corrective action, and providing timely information to management

TABLE 2

Recommended SW-846 Methods for Mercury Analysis

Parameter	Preparation Method*	Analysis Method*
Soils, Solids, and Sediments		
Total Metals	SW-846	7471
TCLP Metals (mercury only)	SW-846	7470
Wastewaters		
Metals (mercury only)	SW-846	7470

*All methods are SW-846 methods unless otherwise specified.

regarding the effectiveness of activities affecting the QA/QC project. A comprehensive system of planned and documented audits shall be carried out to verify compliance with all aspects of the QA/QC project and to determine its effectiveness.

Audits will consist of an evaluation of work areas and activities as well as a review of project documentation. The audits will cover both field and office activities.

The records of all operations will be reviewed to verify that related activities were performed in accordance with appropriate procedures. Items reviewed may include, but are not limited to, calibration records of equipment, daily activity logs, photographs, and all data, logs, and checkprints resulting from the field operations.

Audits will also examine documentation and verification of field and laboratory data and results; performance, documentation, and verification of analyses; preparation and verification of drawings, logs, and tables; content, consistency, and conclusions of reports; compliance project requirements; and maintenance and filing of project records.

Activities of each subcontractor will be audited at least once by an EERC representative to ensure that required equipment and procedures for sample collection, preservation, shipping, handling, laboratory, and documentation will be used.

The quality assurance coordinator is responsible for scheduling, planning and conducting quality audits, issuing audit reports, retaining audit records, and following up on requested corrective action.

9.1 Performance Audits

The laboratories selected to analyze the samples collected for the CSD project may be asked to provide information on any performance samples analyzed during the past two years that are applicable to the project and information on any certifications that they have obtained for

handling samples of similar matrices. Analysis of performance samples, specifically for the CSD project, will not be required.

The EERC participates in state certification programs. The performance audit verifies the ability of the laboratory to correctly identify and quantify compounds in blind check samples submitted by the auditing agency. The purpose of these audits is to identify laboratories capable of generating scientifically sound data. The EERC is certified to perform environmental analyses under programs administered by the North Dakota State Department of Health.

In addition to external audits conducted by certifying agencies, the EERC regularly conducts internal audits to evaluate the facilities, equipment, staff, and procedures needed to produce acceptable data. Also, the EERC routinely analyzes internal check samples as follows:

- Laboratory QA/QC check samples are analyzed at a frequency equal to at least 10 percent of the total number of samples analyzed.

- EPA QA/QC check samples are provided on an annual basis.

The results of these audits are used to identify areas where additional training is needed or clarification of procedures is required.

9.2 System Audits

System audits will be conducted on sampling/analysis at the discretion of the project manager. In addition, the laboratory's SOPs for record keeping may be requested for review by the project manager or a designee. If possible, the manager will audit the laboratory or field operations to determine whether proper record-keeping procedures are used and maintained.

These audits will consist of all or any of the following items:

- Review of the organization and responsibilities to determine the functional operation of the QA/QC project.

- Check on the availability and implementation of standard operating procedures.

- Assessment of traceability of samples and data.

- Validation that the appropriate QA/QC checks are being made and that appropriate documentation is maintained.

- Determination of whether the field and laboratory equipment is available, calibrated, and in proper working condition.

- Assurance that record-keeping procedures, including notebooks, logsheets, bench sheets, and tracking forms, are properly maintained.

- Verification that the appropriate chain of command is followed in responding to variances and implementing corrective action.

- Review of data validation.

- Issuance of blind QA/QC samples to the analytical laboratory for analysis of specified critical parameters.

- Preparation of a QA/QC report that includes the results of the blind QA/QC samples and the associated calibration and control charts (if appropriate) and delivery of the report to the project manager and QA/QC team leader.

9.3 Audit Scheduling

The QA/QC team leader will schedule audits so that all quality procedures and elements are periodically audited. Random, unscheduled audits may supplement the regularly scheduled audits when deemed necessary by the project manager. The QA/QC team leader will periodically evaluate, prepare, and maintain a schedule of audits to be conducted, including follow-up as required, to assure that any deficiencies and/or adverse conditions are documented and properly evaluated, and appropriate corrective action is taken.

9.4 Audit Planning

The QA/QC team leader will determine the objective, scope, general approach, and reference criteria necessary to successfully conduct the audit. The QA/QC team leader will prepare the quality audit planning and audit checklists to be used during the audit.

9.5 Reporting Audit Findings and Obtaining Corrective Action

The QA/QC team leader will:

- Report the audit findings to the project manager and affected personnel to assure validity of findings and make recommendations for corrective action.

- Obtain corrective action commitments from the project manager and affected personnel as appropriate.

- Assure that the commitments identify actions to be taken, individuals responsible, and completion dates and also that the committed actions are reasonable, to prevent recurrence of the discrepancy or significantly reduce the probability of its recurrence.

- Follow up on corrective action commitments to assure their timely accomplishment and effective use.

10.0 CORRECTIVE ACTION

The need for corrective action may be identified during the review of data, field investigation, field and office surveillance and audit, and safety and health surveillance. The identification, correction, verification, and documentation of corrective action is controlled by the

QA/QC project and implementing procedures. Corrective action is controlled by audit findings and action memos.

Data generated as part of the analytical QA/QC project will be sent to the QA/QC team leader and the project manager to ensure the absence of systematic bias or trends. Corrective actions will be taken upon identification of any problems with the project that affect product quality.

10.1 General Procedures

Corrective actions will be taken upon identification of any problems with the project that affect product quality. The project manager or a designee will be responsible for identifying the cause of the problem and developing a solution. The root cause of the problem will first be determined, then the effects of the problem on the program will be identified for subsequent analysis of the effectiveness of the corrective action. The project manager, in conjunction with the QA/QC team leader and an appropriate supervisor (i.e., laboratory coordinator), will develop a viable corrective action. The effects of the action will be tested to determine whether the action eliminates the problem and associated concerns.

After developing a successful corrective action, the project manager, QA/QC team leader, or their designees are responsible for documenting and implementing all corrective actions. A Corrective Action Memorandum will be written, which documents the problem and describes the corrective action that will be implemented, as well as the expected results of implementation. The project manager or a designee will assess the effectiveness of the corrective action after implementation is complete. Copies of the Corrective Action Memorandum will be sent to all personnel who would be affected by the corrective action.

10.2 Performance/System Audits

Data generated for the CSD Program will be reviewed by the QA/QC team leader and the appropriate technical staff to ensure the absence of systematic bias or trends and to ensure that appropriate corrective actions are taken.

Field activities performed by the sampling team will be audited by a third-party representative to ensure that required equipment and procedures for sample collection, preservation, shipping, handling, and documentation are used.

The need for field or laboratory audits and the frequency of such audits will be specified in the SAP.

10.3 Data Outside Control Limits

If at any time the data fall outside previously designated limits, the following actions will be taken:

- If a field/laboratory person observes that instruments are not within calibration limits, the instruments will be recalibrated; samples will be reanalyzed once an acceptable calibration has been obtained.

- If the field/laboratory person or engineering staff observes data problems (for example, if results for specific QA/QC analysis are outside the QA/QC limits), that person will immediately notify the QA/QC team leader.

- If the QA/QC team leader discovers data problems or is notified of a problem, the team leader will decide on the severity of the problem and take the appropriate action:

  — *Minimal Data Problems*. Minimal data problems are defined as problems that occur but will have no impact on the project's data quality objective; e.g., the chain-of-custody sheets were initialed and not signed. The corrective action taken will be documented.

  — *Moderate Data Problems*. Moderate data problems are defined as problems having an impact on the data quality objective but data are still valid; i.e., detection limits for an analyte were between 1 ppm and 2 ppm, and the project manager was not contacted. A problem memorandum will be prepared and sent to the project manager and a decision on the appropriate action will then be made.

  — *Severe Data Problems*. Severe data problems are defined as problems having an impact on the data quality objective and potentially invalidating the data; i.e., samples were run after the holding times had expired. A problem memorandum will be prepared and sent to the project manager, initiating corrective action procedures.

10.4 Data Problems

The project manager will investigate the problem and will be responsible for ensuring that one or more of the following actions is taken:

- If the problem is minimal and occurred in-house, the appropriate person, i.e., lead engineer or laboratory coordinator, will correct the problem and prepare a Corrective Action Memorandum.

- If the problem is limited in scope and easily corrected, the appropriate person, in concert with the project manager, will make the corrections and prepare a Corrective Action Memorandum.

- If the problem is judged by the field sampling staff, laboratory coordinator, or project manager to be significant, corrective actions will be initiated.

10.5 Unusual Occurrences and Unexpected Events

During a field investigation, if a condition is encountered that is totally outside of, or contrary to, that which is anticipated in project planning and not provided for under field investigation procedures, affected work may be stopped. The project manager (and site health and safety officer, if applicable) must immediately be contacted and their direction obtained for the completion of activities. Any such deviation from field planning and procedures is documented in field notebooks and an action memo is prepared. Action memos are prepared by the responsible engineer and processed by the QA/QC team leader. The causes and actions to

prevent recurrence of the deviation are determined and concurred with by the project manager and the QA/QC team leader. The QA/QC team leader tracks the action memo and is responsible for documenting the resolution of the deviation.

10.6 Management Corrective Action and Stop Work

Quality deficiencies serious enough to warrant management action are identified and reported in a management correction action report (MCAR). Conditions requiring management corrective action may be identified by anyone associated with a project. Such conditions are reported to the QA/QC team leader by preparation of a MCAR form. The MCAR identifies the condition adverse to quality, its apparent cause, the corrective action taken, action taken to prevent recurrence, and follow-up verification.

Authority to stop work is given to the health and safety manager, who can suspend work activities that are being conducted in a manner that threatens health, safety, or the environment. Authority to stop work is also given to the QA/QC team leader, who can suspend work activities that jeopardize accomplishment of the project or project quality objectives.

10.7 Laboratory Internal Corrective Action

When errors, deficiencies, or uncontrollable situations exist, the QA/QC project provides "corrective actions" to resolve problems and restore proper functioning to the analytical system.

Corrective actions may be necessary when:

- QA/QC data are outside acceptable precision and accuracy.
- Blanks contain contaminants above acceptable levels.
- Undesirable trends are detected in spike recoveries or relative percent difference between duplicates.
- There are unusual changes in detection limits.
- Deficiencies are detected during internal or external audits, or from the results of performance evaluation samples.
- Inquiries concerning data quality are received from clients.

Corrective action procedures are often handled by the analyst, who reviews the laboratory procedures for possible errors and checks the instrument calibration, spike and calibration mixes, instrument sensitivity, etc. If problems persist or cannot be identified, the matter is referred to the laboratory supervisor for resolution. Once resolved, documentation of the corrective action procedures is filed with the QA/QC team leader. Corrective action documentation is reviewed by the project manager.

11.0 CALIBRATION PROCEDURES

11.1 Laboratory Analysis

All instruments will be calibrated each day that analyses are performed. The calibration standards must include the constituents of concern for the project. The calibration procedures described in the appropriate analytical methods will be followed. In addition, the laboratory must have a SOP for instrument calibration. These SOPs must be available for review upon request.

All calibration information will be documented. If the calibration check standard does not meet the criteria specified in the method, the instrument will be recalibrated and the samples analyzed after the last calibration check standard meeting the calibration specifications. If deviations from or modifications to these procedures are necessary, approval must be obtained from the project manager prior to implementation of the deviation/modification. Documentation of these deviations/modifications and the reason for their implementation must be presented in the final analytical data report.

Calibration standards must be prepared using pure standard materials or purchased as certified solutions. If the standards are made from pure standard materials, the materials must be assayed and the purity of the standard must be known. When compound purity is assayed to be 96 percent or greater, the weight may be used without correction to calculate the concentration of the stock solution unless otherwise specified in the analytical material. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source. If commercially prepared, the name of the manufacturer and the information regarding purity of the standard or the concentration of the stock solution must be available upon request.

Instrument calibration procedures may be followed according to those specified by the manufacturer or according to the procedures provided in Table 3, depending on the situation. The concentrations of the calibration standards for each method will be determined by the detection limit and the linear curve of the range. EERC calibration procedures are described in Appendix A.

11.2 Field Calibration

All instruments will be calibrated each day that analyses are performed in the field. The calibration procedures described in the appropriate SOPs written for the field team and provided in the SAP must be followed. If the calibration check standard does not meet the criteria specified in the method, the use of the instrument will be discontinued until the unit can be recalibrated. Samples analyzed after the last calibration check standard meeting the calibration specifications will be reanalyzed with a calibration instrument, if possible.

Field testing equipment will be subject to periodic inspection and calibration. At a minimum, measuring and test equipment will be calibrated daily, unless specified otherwise by the manufacturer. Calibrated equipment will be identified by using either the manufacturer's serial number or by a permanent tag number assigned to the instrument. A label with the identification number and the date and time of calibration will be attached to the instrument.

TABLE 3

Calibration Procedures for Analytical Instruments

Instrument	Procedure
Flame AA	Daily four-point calibration with blank and appropriate standards. Check standard and blank analysis after every ten samples.
Furnace AA	Daily four-point calibration with blank and appropriate standards. Check standard and blank analysis after every ten samples.
ICP	Daily four-point calibration with blank and appropriate standards. Interference check sample analysis every 8 hours. Check standard and blank analysis after every ten samples.
GC	Meet chromatographic acceptance criteria, then do three-point initial calibration with 0.2-, 0.25-, and 1.0-μg/L standards, followed by daily chromatographic check and calibration check.
GC/MS	Meet MS tuning criteria followed by chromatographic acceptance criteria. Then do three-point initial calibration with 20-, 50-, and 100-ng/mL standard, followed by daily chromatographic check and calibration check.
Analytical Balance	Prior calibration check with Class S weights in the gram and milligram range. Other checks as appropriate in expected weighing range.
HPLC	Meet chromatographic acceptance criteria, then do multipoint initial calibration followed by daily chromatographic check and calibration check.
pH Meter	Three-point calibration at pH 4, 7, and 10. Calibration check after every ten samples.
Conductivity Meter	Calibration check daily and every 20 samples.
UV Spectrometer	Daily multipoint calibration. Check standard every 20 samples.
Technicon	Daily multipoint calibration. Check standard every 20 samples.
TOC	Daily single-point calibration in triplicate. Check standard every 20 samples.
TOX	Daily calibration check. Check standard every 20 samples.
IC	Daily multipoint calibration. Check standard every 20 samples.
Thermometers	Check against NBS thermometer every 6 months.
Hg Analyzer	Daily four-point calibration. Check standard and blank analysis after every ten samples.

Equipment calibration date, time, and comments/observations will be recorded in the field logbook. Malfunctioning equipment will be removed from service and tagged to ensure it is not inadvertently used.

11.3 Calibration Failures

Equipment that fails calibration or becomes inoperable during use will be removed from service and either segregated to prevent inadvertent use or tagged to indicate it is out of calibration. Such equipment will be repaired and recalibrated or replaced as appropriate. The QA/QC team leader shall be notified of all equipment problems for data qualification purposes.

11.4 Calibration Records

In addition to recording all information pertaining to calibration of equipment in the field logbook, equipment calibration records will be prepared and maintained for each piece of measuring and testing equipment to establish calibration procedures and for tracking and ensuring proper and timely calibration.

Calibration records will include the following information:

- Type of equipment
- Identification number of equipment
- Calibration procedure
- Calibration frequency and acceptable tolerances
- Calibration dates and times
- Calibration data
- Name of person performing calibration
- Information on calibration acceptance or failure

12.0 DATA REDUCTION, VALIDATION, AND REPORTING

All analytical data are extensively checked for accuracy and completeness. The data validation process consists of data generation, reduction, and review.

The analyst who generates the analytical data has the prime responsibility for its correctness and completeness. All data are generated and reduced following appropriate protocols. Each analyst reviews the data package to ensure that:

- Sample preparation information is correct and complete.
- Analysis information and analytical results are correct and complete.
- QA/QC results are within established control limits.
- Special sample preparation and analytical requirements have been documented.

The data reduction and validation steps are documented, signed, and dated by the analyst. The analyst then passes the data package to the supervisor and to the QA/QC team leader for review.

For data to be scientifically valid, legally defensible, and comparable, valid procedures must be used to prepare those data. These reporting procedures follow.

12.1 Data Reduction

The analytical laboratory will specify its data reduction methods. A deliverable checklist will be filled out during data review to ensure completeness of data.

Wherever possible, the initial data reduction will be computerized. This reduces the frequency of transcription errors and calculation errors. Where data reduction is not computerized, calculations will be performed in permanently bound laboratory notebooks with carbon copy pages, or on preprinted data reduction pages. The data reduction for some analyses includes analysts' interpretations of the raw data and manual calculations. When this is required, the analysts' decisions will be written in ink on the raw data sheets. Any corrections to data sheets will be made by lining out inaccurate information, initialing the lineout, and adding the revised information next to the lineout.

12.2 Data Validation

Data validation begins with the analyst and continues until the data are reported. The individual analysts will verify the completion of the appropriate data forms to verify the completeness and correctness of data acquisition and reduction. The laboratory supervisor will review computer and manual data reduction results and will inspect laboratory notebooks and data sheets to verify data reduction correctness and completeness and to ensure close adherence to the specified analytical method protocols. Calibration and QA/QC data will be examined by the individual analysts and the laboratory supervisor to verify that all instrument systems are working properly and that QA/QC objectives for precision, accuracy, completeness, and method detection limits are being met.

The principal criteria that will be used to determine the validity of data generated during collection and reporting are:

- Verification, on a weekly basis, by the project analyst, that all raw data generated in the preceding week have been stored on computer disk and on hard copy and that storage locations have been documented in the laboratory records.

- Examination of all the data by the analytical coordinator to verify adequacy of documentation and to confirm that peak shape, resolution, and calculations or response factors of shift standards match calibration curves.

- Confirmation that raw areas for internal standards and calibration standards and raw and relative areas for surrogate compounds are within the expected values.

- Reporting of all associated blank standards, calibration standards, check standards, and QA/QC data (matrix spike, matrix spike duplicate, etc.) with the analytical results of each batch of samples.

- Reporting of all analytical data for samples with no values rejected as outliers.

QA/QC outlier data are defined as those QA/QC data lying outside a specific QA/QC objective window for precision or accuracy for a given analytical method (e.g., matrix spike data showing recoveries below 20 percent). Should QA/QC data be outside of the control limits, the laboratory supervisor will investigate the cause of the problem, have the QA/QC data flagged with a data qualifier, and notify the project manager and the QA/QC team leader. If the data must be reanalyzed and the reanalysis corrects the problem, then only the reanalysis results will be reported. If both initial analysis and reanalysis results indicate that a matrix problem exists, both results will be reported, and the results will be qualified in the final data package. If reanalysis is not feasible, the initial analysis results will be reported and qualified in the laboratory's final data package.

12.3 Reporting

A variety of reporting formats may be used. In general, reports will consist of a copy of the sample logsheet, chain-of-custody and analytical data. Case narratives are included when necessary to explain any problems encountered or when general comments are required.

Data are reported by sample or by test. Pertinent information, including dates samples were obtained, received, prepared, and extracted, are included on each report. The analytical methodology used is also reported. The method reporting limit and regulatory limit, if appropriate, for each analysis is normally reported for the majority of analyses.

Results of any matrix spikes and duplicates, or other project-specific QA/QC parameters are also reported. All results will be reported to the project manager or a designee by sample batch and will be certified by the laboratory. All reports and documentation required, including chromatograms and mass spectra, calibration records, and QA/QC results, will be clearly labeled with the laboratory sample number and associated field sample number.

Analytical data will be reported on an as-received basis. Analytical results will be given in standard units, as specified by the analytical methods. If reporting units are not specified in the methods, data from the analysis will be reported in $\mu g/L$ for all liquid samples and in mg/kg on an as-received basis for soils and other solid matrices. In addition to the analytical results and QA/QC data, details regarding the corrective actions taken and a discussion of any necessary modifications of the protocols established in the referenced methods will be included in the final data report.

The final data package submitted by the analytical laboratory must include a summary of the analytical results for each sample, as well as all reports and documentation generated as required by the analytical methods (i.e., chromatograms, extraction notes, and chain-of-custody forms).

When the analytical data reports are received from the laboratory, the project manager, QA/QC team leader, and engineering staff will review the data and incorporate the data into the characterization report/OER. The characterization report/OER will be reviewed by the principal engineer designated for the project, the QA/QC team leader, and the project manager prior to submittal of the report. The report will then be reviewed.

13.0 PREVENTIVE MAINTENANCE

To minimize downtime and interruption of analytical work, preventive maintenance is routinely performed on each analytical instrument. Routine maintenance is performed for all major instrumentation by the operator under supervision of the area supervisor. When repairs are necessary, they are performed by either the operator, supervisor, or trained service engineers employed by the instrument manufacturer. Service contracts with the instrument manufacturers are maintained on the major sophisticated instrumentation. These contracts also provide for preventive maintenance.

Preventive maintenance procedures are maintained by each supervisor. Logbooks are used to document the preventive maintenance and repairs performed on each analytical instrument. All laboratory instrumentation and field equipment must be maintained following procedures outlined by the manufacturer.

13.1 Field Preventive Maintenance

Prior to a sampling project, field equipment must be inspected and calibrated to ensure that it is working properly. Spare parts must be available and will be taken on the sampling trip. Following the field equipment's use, it must be decontaminated using the appropriate cleaning procedures required for the project.

13.2 Laboratory Preventive Maintenance

Instrument maintenance logbooks will be kept with each instrument and will be updated by the operator whenever either routine or nonroutine maintenance procedures are performed. Laboratory personnel will be responsible for the daily recording of refrigerator and freezer temperatures and the calibration of a variety of equipment, including, but not limited to, pH meters, balances, thermometers, and thermocouples. Scheduled periodic measurements will be performed (and documentation prepared) for oven and incubator temperatures and fume hood air flow rates. Expendable materials will be replaced at recommended intervals, such as vacuum pump oil and air filters on instrumentation cooled by forced air supplies. Cleaning and lubrication of serviceable parts will also be performed following specific guidelines established by the instrument manufacturers. Spare parts or backup equipment will be maintained.

14.0 QA/QC REPORTS TO MANAGEMENT

The project manager, in conjunction with the QA/QC team leader, will identify critical areas of the project that will be subject to inspection. These inspections will be performed by qualified staff members who are not performing or supervising the activity. In addition, the principal CSD work group members may request auditing and/or review of the field activities, laboratory activities, or analytical data to be completed by their designated QA/QC team leaders. The areas inspected may include staff qualifications, equipment maintenance records, equipment calibration records, protocol adherence, documentation practices, sample traceability and control, data traceability and document control, record keeping practices, review and validation practices, computation practices, QA/QC data and practices, and QA/QC compliance.

The results of inspections, audits, summaries of problems, and corrective action requests will be reported to the project manager as they are available or as they are specified in the technology-specific SAPs.

Reports for the CSD Program, e.g., characterization reports and OERs, will include a separate QA/QC section that documents the QA/QC activities that lend support to the credibility of the data and the validity of the conclusions.

The QA/QC section will include the following:

- Changes to procedures outlined in this QA/QC project plan.
- Limitations or constraints on the applicability of the data.
- The status of QA/QC programs, accomplishments, and corrective actions.
- Results of technical systems and/or performance evaluation QA/QC audits.
- Assessments of data quality in terms of precision, accuracy, completeness, method detection limit, representativeness, and comparability.

15.0 REFERENCES

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ATTACHMENT A

EERC ARL QUALITY ASSURANCE-QUALITY CONTROL

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QUALITY ASSURANCE-QUALITY CONTROL

1.0 INTRODUCTION

The Analytical Research Laboratory (ARL) is one of a number of research laboratories accociated with the Energy and Environmental Research Center (EERC) in Grand Forks, North Dakota.

Within this framework, the Applied Chemistry area strives to apply chemical concepts and methodologies to solve a wide variety of problems, including materials characterization, metals extraction, determination of groundwater-sediment interactions, waste-groundwater interactions, diesel fuel production from vegetable oil, and the chemical characterization of groundwater. Moreover, other EERC research programs rely extensively on the practical expertise developed in the course of applied-chemistry research.

Quality assurance (QA) at the ARL encompasses the entire range of activities associated with sample collection, sample preservation, chemical analyses, and data reporting with emphasis on procedures for assessment, prevention, and correction. The principal components of the ARL QA plan reside in the quality control program. This program is supervised at both the corporate and laboratory level and is accomplished through clearly defined objectives, documented procedures, management support, and a comprehensive audit system. The following sections outline systems which substantiate and document that data produced in the laboratory are of proven and known quality.

2.0 QUALITY ASSURANCE POLICY

The policy of the ARL is to conduct sufficient quality assurance activities to demonstrate that all data generated by the laboratory are scientifically valid, defensible, and of known precision and accuracy. Data must be complete, representative, and comparable. Data must meet QA requirements set by the North Dakota State Department of Health and Consolidated Laboratories.

Dave Hassett, the director of the EERC Analytical Research Laboratory, has overall responsibility for the development, implementation, and continued operation of the QA program. The director is responsible for identifying equipment, personnel, and training needs, and coordinating and discussing these needs with appropriate state personnel.

3.0 STANDARD OPERATING PROCEDURES

Details of the analytical and QA protocols are contained in a set of standard operating procedures (SOPs). SOPs incorporate the requirements of the analytical methods, the QA program, and good laboratory practices. Examples of some typical SOPs are given below.

3.1 Method SOP

a. Project and method requirements: detection limits, blanks, spikes, and duplicates

b. Reagent and standard preparation

c. Equipment and glassware requirements

d. Sample preparation

e. Sample analysis: instrument calibration, standard, samples

f. Data and report generation

g. Data and report approval

h. Sample return/disposal

3.2 Instrument SOP

a. Operational protocols: start-up, settings, calibration, and shutdown

b. Maintenance and service

c. Sample log and service log

3.3 Sample Control SOP

a. Receiving information

b. Log in/storage

c. Chain-of-custody

d. Sample transfer/disposal

4.0 AUDITS AND PERFORMANCE EVALUATIONS

4.1 External Performance Audits

The EERC's ARL is certified to perform analyses on mercury by the North Dakota State Department of Health and Consolidated Laboratories, using EPA Method 245.1, Cold Vapor Atomic Absorption. See Figure A-1.

4.2 Internal Performance Audits

The purpose of internal laboratory auditing is to identify the sources of measurement error. Some of the potential error sources are the analyst, equipment, the calibration, and the operating conditions.

Internal quality is maintained through the following exercises:

- Laboratory QC check samples are analyzed at a frequency equal to at least 10% of the total number of samples.
- Matrix-matched spiked samples are analyzed at a frequency equal to at least 10% of the total number of samples.
- Duplicate samples are analyzed at a frequency equal to at least 10% of the total number of samples.
- Atomic absorbances of standards are recorded each time an analysis is performed.

5.0 SAMPLE COLLECTION AND PRESERVATION

The majority of samples received by the EERC's ARL are collected in the field by our own experienced sampling teams. The ARL provides properly cleaned sample containers of appropriate size and construction, and containing proper preservatives, if necessary, to ensure the successful transportation of samples. A list of proper containers and preservatives is provided in Figure A-2.

6.0 SAMPLE CHAIN-OF-CUSTODY

A sample is physical evidence collected from a facility or from the environment, and possession must be traceable from the time of sample collection, throughout the laboratory analysis, and up to sample disposal. Samples received by the ARL follow an orderly chain-of-custody as follows.

Upon receipt, samples are checked for closure integrity, label identification, quantity verification, and any discrepancies. Samples are then assigned a unique laboratory number, recorded in the laboratory logbook (Figure A-3) with all essential sample information, and the designated laboratory number is placed directly on the sample container. Samples are stored appropriately within the laboratory during sample analysis. The laboratory is locked during the night with only authorized laboratory personnel having access. Daytime access to the laboratory is through a monitored reception area.

NORTH DAKOTA STATE DEPARTMENT OF HEALTH AND CONSOLIDATED LABORATORIES

CERTIFICATE OF ACCREDITATION

UND Energy and Environmental Research Center - Grand Forks, ND

meets acceptable standards for the performance of the following analyses:

All parameters on the most recent dated list

Director, Consolidated Laboratories

Certification Officer

This certificate remains the property of the North Dakota State Department of Health and Consolidated Laboratories and may be removed, for cause, at any time by the Department.

Certificate Number: 88-0030-C Expiration Date: October 31, 1994

Date of Issue: October 25, 1991

List of Certified Parameters for
UND Energy and Environmental Research Center Water Analysis Laboratory
Issued by:
The Chemistry Division of
The North Dakota State Department of Health and Consolidated Laboratories
October 25, 1991

Alkalinity (total), Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, COD, Iron, Lead, Magnesium, Manganese, Mercury, Molybdenum, Nickel, pH, Potassium, Selenium, Silver, Sodium, Specific Conductivity, Strontium, Sulfate, Thallium, Titanium, Total Dissolved Solids, Vanadium, Zinc.

7.0 REAGENT AND STANDARDS

A critical element in the generation of quality data is the purity/quality of the reagents and standard solutions used in analytical operation. Contaminated or improperly prepared reagents or calibration standard solutions can cause errors in analytical results.

All primary mercury reference standards and mercury check standards are those recommended by or obtained through the National Institute of Standards and Technology (NIST) or other reliable commercial sources. All standards are validated prior to use and checked regularly for signs of deterioration, such as discoloration, formation of precipitates, etc. All standards are dated upon receipt, stored, and handled properly, and note is taken of the limited shelf life.

Chemical reagents used in mercury analysis are of analytical grade or better. Chemical reagents are dated upon receipt, stored, and handled properly, and note is taken of those with limited shelf life. Water used to make standards is 10 mega-ohm deionized water equivalent or superior to ASTM Type II water.

8.0 INSTRUMENT CALIBRATION

Calibration of instruments is required to ensure that the analytical system is operating correctly and functioning at the proper sensitivity to meet established detection limits. The atomic absorption spectrophotometer is calibrated each time mercury samples are run with appropriate standard solutions based on the expected range of sample concentration(s). If a check standard fails, the instrument must be recalibrated and samples from the last successful check standard through the failed check standard rerun before sample analysis can continue. Standard absorbances are recorded in the laboratory notebook for comparison with previous standard absorbances to check instrument performance for known standards.

9.0 INSTRUMENT PREVENTIVE MAINTENANCE

Preventive maintenance is an orderly program of positive actions (equipment cleaning, lubrication, reconditioning, adjustment, and testing) for preventing failure of equipment or parts during use. The main objective of the preventive maintenance program at the ARL is to increase the system reliability and thereby decrease downtime and further ensure data precision.

A manufacturer service contract is maintained on the atomic absorption unit used to analyze for mercury as an ongoing part of the preventive maintenance program. All maintenance performed by the analyst is recorded in the laboratory notebook for future reference. When repair or service is necessary, it is performed by a trained service engineer employed by the instrument manufacturer.

Parameter	Method No. Test Code	Matrix	Container	Preservative
ICP Scan	200.7	Water	500 mL poly bottle	HNO_3 to pH ≤ 2.0
	6010	Soil/Waste	Core tube or glass jar	None
Arsenic (GF-AA)	206.2	Water	500 mL poly bottle	HNO_3 to pH ≤ 2.0
	7060	Soil/Waste	Core tube or glass jar	None
Mercury (CV-AA)	245.1	Water	Teflon™ bottle	2% BrCl
analysis only	7470	Soil/Waste	Core tube or glass jar	None
Selenium (GF-AA)	270.2	Water	500 mL poly bottle	HNO_3 to pH ≤ 2.0
	7740	Soil/Waste	Core tube or glass jar	None
Thallium (GF-AA)	279.2	Water	500 mL poly bottle	HNO_3 to pH ≤ 2.0
	7841	Soil/Waste	Core tube or glass jar	None
Lead (GF-AA)	239.2	Water	500 mL poly bottle	HNO_3 to pH ≤ 2.0
	7421	Soil/Waste	Core tube or glass jar	None
Total Cyanide	335.2	Water	500 mL poly bottle	4°C NaOH to pH ≤ 2.0
	335.2-S	Soil/Waste	Core tube or glass jar	None

Figure A-2. Inorganics.

TITLE Log book - Chain-of-Custody

Project No. _____
Book No. _____

From Page No.

Date	Submitter	Initial	Sx Information	Fund #	Lab #

To Page No.

Witnessed & Understood by me,	Date	Investigated by Recorded by	Date	

Figure A-3. Logbook chain-of-custody.

10.0 INTERNAL QUALITY CONTROL

10.1 Duplicate Sample Analysis

In order to ensure that adequate levels of precision are maintained by the EERC's ARL, random duplicate samples are analyzed at a rate of one in every ten samples with at least one duplicate analysis per run and one duplicate per sample matrix.

10.2 Spiked Sample Analysis

In order to account for background contamination and/or sample interferences, spiked sample analyses will be performed on ten percent of all samples. Accuracy is reported as percent recovery of the spike added:

$$\% \text{ Recovery} = \frac{(\text{Sample} + \text{Spike}) - (\text{Sample})}{\text{Spike}} \times 100$$

The spike added should be approximately equal to the expected amount of mercury present in the sample or sample aliquot.

10.3 Corrective Action Protocol

When a situation is determined to be out of control through significant duplicate differences or through spike recoveries of less than 90%, the analyst will rerun the duplicate or spiked samples to reject the actual analysis as a possible source of error. If the error is not at this point, the spike or duplicate should be reprepared to determine if the problem is in sample preparation. If the error is again not found at this point, the next step is to reprepare the standards and the standard curve. If the curve is significantly different from the previous curve, the samples should be rerun, and if the quality control data now show the system to be in control, note should be made in the laboratory notebook when recording data. If the curve is not significantly different, the samples must be rerun by methods of standard additions, and this should bring the system into control; however, if it does not, the lab director should be contacted.

11.0 ANALYTICAL PROTOCOL FOR DETERMINATION OF MERCURY BY COLD-VAPOR ATOMIC ABSORPTION

11.1 Purpose and Application

This method is applicable to drinking, surface, and saline waters and domestic and industrial wastes to determine the amount of mercury in them. The detection limit for a 10-mL sample is 0.1 μg/L.

11.2 Summary of Method

This flameless atomic absorption procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and

aerated from solution. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration.

11.3 Interferences

1. Possible interference by sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the determination of mercury.

2. Interference can occur when copper concentrations exceed 10 mg/L.

3. Sea waters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine, which will also absorb radiation at 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent (25 mL). In addition, the dead air space in the vessel must be purged before the addition of stannous chloride. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

4. Interference from certain volatile organic materials that will absorb at this wavelength is also possible.

5. In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold-vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to ensure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water, the heat step is not necessary.

11.4 Apparatus and Materials

1. Atomic absorption spectrophotometer

2. Leeman PS 200 mercury analyzer

3. Analytical balance

4. Volumetric flasks

5. Graduated cylinders

6. Eppendorf pipet

7. Dry block heater

11.5 Reagents

1. Deionized water

2. Sulfuric acid (concentrated, H_2SO_4)

3. Nitric acid (concentrated, HNO_3)

4. 5% potassium permanganate solution (W/V): Dissolve 50 of potassium permanganate in water and dilute to 1 L.

5. 5% potassium persulfate solution (W/V): Dissolve 50 g of $K_2S_2O_8$ in water and dilute to 1 L.

6. 4% hydroxylamine hydrochloride solution (W/V): Dissolve 40 g of hydroxylamine hydrochloride in water and dilute to 1 L.

7. 10% stannous chloride solution (W/V): dissolve 100 g of $SnCl_2$ in water containing 40 mL of concentrated hydrochloric acid (HCl) and dilute to 1 L. On aging, this solution decomposes. If a suspension forms, mix reagent before use. Make fresh before each use; usually 250 mL is sufficient.

8. Stock mercury atomic absorption standard solution, 1000 ppm.

9. Working mercury standard, 1 ppm:

   - Add 0.1 mL of the 1000-ppm stock mercury standard solution to a 100-mL volumetric flask containing 90 mL of deionized water + 200 μL of HNO_3.
   - Dilute to volume with deionized water and mix well.
   - Prepare fresh daily.

10. Working mercury spike: prepare as indicated above using a different stock mercury standard.

11.6 Sample Handling and Preservation

1. Samples should be preserved by acidification with a 2% bromine monochloride solution to a pH of 2 or lower immediately at time of collection.

2. Holding time: 28 days.

11.7 Calibration and Standardization

1. Using a transfer pipet, transfer 10 mL of deionized water into a series of 50-mL reaction vessels.

2. Add an aliquot of the working mercury standard solution to each vessel.

Aliquot Added, µL	Concentration, mg/L
0	0
20	0.0002
50	0.0005
100	0.001
300	0.003
500	0.005

3. Mix each solution thoroughly by swirling the vessel.

4. Proceed to Step 2 under "Procedure."

11.8 Procedure

1. Using a transfer pipet, pipet 10 mL of each sample into separate reaction vessels.

2. Add 0.5 mL of concentrated H_2SO_4 and 0.25 mL of concentrated HNO_3 to each bottle and swirl to mix.

3. Add 5 mL of the 5% potassium permanganate solution to each vessel and swirl to mix.

4. Allow bottles to stand for 15 minutes. If the permanganate color disappears before 15 minutes, add additional KMO_4 until the permanganate color persists for at least 15 minutes.

5. Add 0.8 mL of the 5% potassium persulfate solution to each bottle and swirl to mix. Stopper bottles.

6. Place the bottles in a dry block heater (maintained at a temperature of 95°C) and heat for 2 hours. Monitor temperature with immersion thermometer. Cover bath.

7. Remove the bottles from the water bath and allow them to cool to room temperature.

8. Add 0.5 mL of the 4% hydroxylamine hydrochloride solution to each bottle and wait until the solution has decolorized (at least 30 seconds). Remove dead air space by blowing air into each bottle.

9. Analyze each standard and sample bottle individually using standard Leeman operating protocol.

11.9 Calculations and Report

1. Construct a curve by plotting the absorbance readings of the standards against the concentration of the standards in milligrams (mg) of mercury.

2. Compare each sample's maximum absorbance value to the standard curve.

3. Calculate the mercury concentration in the sample by the formula:
$$\text{mg Hg/L} = \frac{\text{(mg Hg in aliquot of sample) (1000)}}{\text{volume of aliquot in mL}}$$

4. Report mercury concentration as < 0.002 mg/L if the concentration of the sample is below 0.002 mg/L.

5. As an alternative to the above calculation, a calculator employing linear regression may be used to determine the mercury concentration of the samples.

11.10 Quality Control

1. Spike and duplicate 10% of all samples analyzed, with a minimum of one spike and one duplicate per run.

2. Whenever possible, an EPA audit check sample should be run with each analysis. Recovered mercury concentration of this sample must be within acceptable limits.

11.11 Documentation

1. All information and values are recorded on a worklist.

2. Parameter information is saved.

3. Printouts of data for standards and samples are saved.

11.12 Records

1. Worklists and parameter information are stored in the Mercury Logbook.

11.13 References

1. Methods for Chemical Analysis of Water and Wastes (EPA-600/4-79-020), March 1979, Method 245.1.

2. Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989, Method 3112 B, pg. 3-29 to 3-31.

12.0 DATA REDUCTION, VALIDATION, AND REPORTING

All data is reviewed first by the analyst to ensure that it is complete; precision, accuracy, and detection limits have been met; interpretation of raw data and calculations are correct; contractual requirements have been fulfilled; and, finally, all information is well documented. Data is then compiled and reduced into a standard report form which is inspected by the lab director before it is considered for client use (Figure A-4).

Documentation of analytical and procedural information is part of the quality assurance program. The following describes different types of documentation used in the EERC's ARL:

- SOPs for analytical method performance; standards and reagents preparation; equipment operation, calibration, and maintenance; and general laboratory procedures.

- Laboratory notebooks for documenting raw data and unusual observations or occurrences in the analysis of samples, or in methods development.

- Project files for storing documents associated with the project, including correspondence from the client, chain-of-custody records, project log sheets, raw data, QC data, and a copy of the final report.

ANALYSIS REPORT FORM

REQUESTOR _____
PROJ. # _____
SAMPLE INFO _____
DATE SUBMITTED _____

SAMPLE ID.							
	1	2	3	4	5	6	7
LAB #							
PARAMETER							

DATE REPORTED _____

REPORTED BY _____
DISTRIBUTION _____

Figure A-4. Analysis report form.

DATE FILMED

10/24/94

END