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**Sour Gas Plant Remediation Technology
Research and Demonstration Project
Task 7.53**

**Topical Report
January - December 1993**

**Daniel J. Stepan
Vit Kühnel
Craig R. Schmit**

February 1994

Work Performed Under Cooperative Agreement No.: DE-FC21-86MC10637

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

**By
University of North Dakota
Energy and Environmental Research Center
Grand Forks, North Dakota**

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15 North 23rd Street
Grand Forks, North Dakota 58203**

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EXECUTIVE SUMMARY

Recognizing the potential impacts of sour gas plant operations on the subsurface environment, the Canadian Association of Petroleum Producers (CAPP) and Environment Canada initiated a multiphase study focusing on research related to the development and demonstration of remedial technologies for soil and groundwater contamination at these facilities.

Research performed under this project was designed to supplement and be coordinated with research activities being conducted at an operational sour gas plant located in Rocky Mountain House, Alberta, Canada. These research tasks included hydrogeological site characterization, subsurface contaminant characterization, ex situ treatment of groundwater, and subsurface remediation of residual contamination in the unsaturated zone.

Ex situ treatment of groundwater included evaluations of air stripping, steam stripping, advanced oxidation, and biological treatment, as well as the development of an artificial freeze crystallization process. Soil vapor extraction was evaluated as a technique to address residual contamination in the unsaturated zone.

SOUR GAS PLANT REMEDIATION TECHNOLOGY RESEARCH AND DEMONSTRATION PROJECT

1.0 BACKGROUND

Recognizing the potential impacts of sour gas plant operations on the subsurface environment, the Canadian Association of Petroleum Producers (CAPP) and Environment Canada initiated a multiphase study focusing on research related to the development and demonstration of remedial technologies for soil and groundwater contamination at these facilities. The first phase of the project was completed in 1990 and consisted of a comprehensive review of all soil and groundwater monitoring data submitted to Alberta Environment by sour gas plants in accordance with the Canadian Clean Water Act. That review indicated that all but one of the 45 sour gas plants, for which data were available, exhibited some form of impact on soil and groundwater quality. The study identified the most frequently occurring contamination situations at the sites and classified them as to sources and types of contaminants and hydrogeological characteristics of the contaminated setting.

The next phase of the study consisted of a detailed review of available subsurface remedial technologies that could be applied to specific identified problems. Established and innovative technologies were assessed, and those with the most promise for dealing with the type of contamination situations present at sour gas processing facilities were recommended for further development and/or demonstration.

This current research at the Energy & Environmental Research Center (EERC) is in response to the direction provided in the previous phase. By demonstrating not only appropriate new technologies and techniques, but also approach and methodology, the present activities and their documentation will assist industry in selecting and applying remediation technologies that will most efficiently, effectively, and economically solve their contamination problems at the sites in question.

2.0 EX SITU GROUNDWATER REMEDIATION RESEARCH

Research related to ex situ groundwater remediation involves a number of interdependent research activities to assess and optimize pump-and-treat operations at these sites. Specific areas of research include the study of aquifer response to pump-and-treat operations in a complex system, upgrading and optimizing the pump-and-treat system that presently exists at the site, and development and demonstration of innovative remediation technologies, such as advanced oxidation processes, biological treatment processes, and freeze crystallization.

2.1 Air Stripping

Air stripping is a physical treatment process used to remove volatile compounds from water. The process utilizes a countercurrent flow of water and air in a packed column, transferring volatile compounds from contaminated waters to air based on mass transfer principles across gas-liquid interfaces.

The complex mixture of compounds found in the groundwater at the Strachan Gas Plant have created scaling and operational problems with the pump-and-treat system that presently exists at the site. A process flow diagram for the modified pretreatment system and air stripping process is shown in Figure 1. The overall process consists of an oil/water separator to remove free-phase condensate; permanganate treatment followed by filtration for iron removal; water softening to remove hardness and scale-forming constituents; and air stripping for the removal of dissolved volatile organics, including benzene, toluene, ethylbenzene, and xylenes (BTEX). Influent to the system consists of groundwater pumped from recovery wells RW-8 and RW-13, which are combined prior to treatment.

Figure 1. Flow diagram for the modified pump-and-treat system at the Strachan Gas Plant.

Research efforts were directed primarily towards reduction of scale formation, as well as air stripper optimization, oil/water separation, and optimization of filter operation and backwash cycles. These efforts are being coordinated with the chemical characterization study and will include field trials of appropriate remedies and subsequent upgrades.

One of the two groundwater recovery wells in operation, RW-13, has been producing very fine, suspended, black particles, of unknown composition. RW-13 had to be taken out of operation because of severe fouling of the existing pump-and-treat system. Efforts to identify the black material were conducted using x-ray fluorescence (XRF) to determine bulk chemistry, x-ray diffraction (XRD) to determine the mineralogy, and scanning electron microscopy (SEM) to determine mineral composition. A discussion of the composition of the black material is presented in Section 4.0 of this report. Future efforts will include research related to the effective removal of the material prior to air stripping.

2.2 Advanced Oxidation

Advanced oxidation is a chemical treatment process that uses oxygen from sources such as ozone (O_3) and hydrogen peroxide (H_2O_2) to oxidize organic constituents that are dissolved in water. The process may be coupled with ultraviolet light, which serves as a catalyst in the destruction of organic compounds. Carbon dioxide (CO_2) and water are the end products of the oxidation reactions.

Advanced oxidation processes were evaluated as a treatment alternative for the removal of organic compounds from contaminated groundwater produced during pumping, as well as offgases produced from air stripping and soil vapor extraction.

During bench-scale studies, suspended solids were removed by gravity settling prior to treatment in a stainless steel Rayox oxidation reactor. The samples were pH-adjusted, the ultraviolet light was activated, and hydrogen peroxide (H_2O_2) was added. Laboratory studies showed that advanced oxidation is capable of reducing BTEX in the Strachan groundwater to less than 5 $\mu\text{g/L}$ within a 30-minute contact period.

Pilot-scale advanced oxidation trials were conducted on-site at the Strachan Gas Plant. Results of these trials indicated that greater than 99% removal efficiencies were achieved under optimal operating conditions, with treated effluent containing less than 10 $\mu\text{g/L}$ of each of the BTEX compounds.

2.3 Steam Stripping

Steam stripping is a physical treatment process used to remove volatile and semivolatile organics or dissolved gases from water. Steam stripping is based on the volatility of the constituents being stripped relative to the volatility of water. This technology uses a countercurrent flow of water and steam in a packed column to provide adequate contact between liquid (groundwater) and vapor (steam). The condensate, along with contaminants, is condensed, collected, and subjected to treatment or disposal.

Bench-scale steam stripping experiments were conducted using a glass column filled with Raschig rings to enhance liquid-vapor contact. The tests showed a BTEX removal efficiency of 99.7% during operation at pH 6.9 and a liquid-to-vapor ratio of 5:1.

Significantly lower removal efficiencies were observed during operation at pH 5 and were attributed to higher stability of BTEX compounds at the lower pH. However, scaling from the deposition of calcium carbonate, iron oxide, and manganese oxide was reduced during operation at the lower pH.

Pilot-scale steam stripping trials were conducted on-site at the Strachan Gas Plant. During the trials, groundwater feed rate and steam flow rate were varied to accommodate groundwater-to-steam ratios from 5 to 14. Additionally, the pH of the groundwater was varied between 4.5 to 9.0. Under all experimental conditions, the treated groundwater contained less than 10 $\mu\text{g/L}$ of the respective BTEX compounds. The overhead condensate stream from the stripping tower, including BTEX and other volatile contaminants, was processed in the advanced oxidation unit to destroy the contaminants and avoid waste production.

2.4 Biological Treatment

Biological treatment is used to remove biodegradable organic compounds and certain inorganic compounds, such as ammonia, from water. Biological processes utilize microorganisms to biochemically oxidize dissolved organic matter to CO_2 , water, and other end products, such as NO_3^- and PO_4^{3-} .

Bench-scale biological treatability testing of groundwater samples collected from the Strachan site was performed. Because of the presence of volatile organics, amines, and amine degradation products, a coupled, attached-growth, nitrification–denitrification system was selected for evaluation. The treatment system consisted of a two-stage rotating biological contactor. Figure 2 is a conceptual diagram of the coupled nitrification–denitrification process. Groundwater contaminated with organics and ammonia provides influent to the system. The removal of organic compounds and the reduction of nitrate to nitrogen gas (denitrification) is accomplished in the first stage (anoxic reactor). Stage 2 is an oxic reactor where ammonia is biochemically oxidized to nitrite and nitrate (nitrification). Recycle between the two stages provides the removal of both carbonaceous and nitrogenous contaminants in a single treatment system.

Figure 2. Conceptual diagram of the coupled nitrification–denitrification process.

Microbial seed for biological treatability testing was developed from soil samples collected at the Strachan site. Testing with the Strachan soil microbes was intended to provide insight into the natural biodegradation of contaminants at the site, as well as the potential for the application of in situ bioremediation.

The goals of biological treatability testing were to 1) evaluate the removal of organic contaminants to target levels, 2) demonstrate biological nitrification (ammonia oxidation), and 3) demonstrate denitrification of nitrified effluents.

Because of start-up delays resulting from complications in receiving groundwater samples for testing, supplemental contaminant characterization activities that were required to develop soundly-based treatment were delayed. As a result of these delays and the time required for microbial acclimation and stabilization, not all of the goals of the biological treatment assessment were achieved. The system will be continued in operation as part of subsequent testing. Average results of testing to date are summarized in Table 1. Biological nitrification has developed in the attached growth system, as indicated by the reduction of ammonia with accompanying increases in nitrate. Since the reduction in ammonia does not balance stoichiometrically with the increase in nitrate, it appears as though a certain amount of denitrification is also occurring. Organics removal, as measured by chemical oxygen demand (COD), has consistently remained at approximately 35 percent. The remaining COD can be attributed to biorefractory organics.

2.5 Freeze Crystallization

Freeze crystallization for the separation of contaminants from the groundwater at the Strachan site will be evaluated as a treatment alternative to the more standard pump-and-treat approach that is presently in operation. Water purification by freeze-thaw cycling can be explained by basic thermodynamics and crystallization theory.

Thermodynamics indicate that as contaminants are dissolved in water, the freezing point of the solution is lower than the 32°F that is required to freeze pure water. However, if a contaminated water solution is cooled below 32°F, but not below the freezing point of the contaminated solution, partial freezing of the solution occurs. Under

TABLE 1

Summary of Bench-Scale Biological Groundwater Treatment Results

Parameter (mg/L)	Influent (mg/L)	Stage 1 Effluent (mg/L)	Stage 2 Effluent (mg/L)
Chemical Oxygen Demand	115	76	76
Ammonia	52	45	42
Nitrite	< 1	< 1	< 1
Nitrate	20	18	16

these conditions, the freezing of water in the solution results in the formation of relatively pure ice and a more concentrated contaminant solution. This simple process can be used to produce either pure water or to concentrate chemical compounds in solution.

When contaminated water begins to freeze, it initially forms crystals of pure water, and an aqueous solution, having elevated concentrations of contaminants, is distributed in the space between the crystals. If freezing is rapid, crystals are smaller than if freezing occurs slowly. Thus crystals formed slowly, at temperatures just below 32°F, are largest. The size of the crystals formed determines the amount of space between the crystals, with large crystals having more space between them than small crystals. This can be observed by measuring the permeability of various ice packs. Since the density of the water with elevated contaminant concentrations is greater than the density of the ice, the water readily flows through a permeable ice pack. Thus the aqueous solution, with elevated contaminant values, is readily separated from a permeable ice pack.

The development and evaluation of an artificial freeze crystallization process were conducted by the Resource Technology Corporation (RTC) of Laramie, Wyoming, under a subcontract from the University of North Dakota Energy & Environmental Research Center (EERC). Previous research indicates freeze crystallization processes are potentially applicable to waters with a wide variety of mixed contaminants, consume less energy than distillation or evaporation processes, and do not require chemicals for water purification.

The process developed uses artificial refrigeration to freeze and subsequently purify the contaminated groundwater. This process is similar to commercially available freeze-crystallization water purification processes successfully in use in the United States and Canada. However, the design of this unit is such that capital equipment requirements are expected to be dramatically reduced compared to existing commercial units. Once successfully developed and demonstrated, the equipment design should result in reduced capital costs, reduced labor, reduced space requirements, and improved operation.

This process design was conceptualized by RTC and the EERC. The research to develop this treatment process included the construction of a prototype unit and experimental process evaluation. Subsequent research will provide a demonstration and prove-in of the prototype unit at the Strachan gas plant, followed by process scaleup and economic evaluation.

The general objective of this research was to develop cost-effective and viable processes utilizing freeze crystallization technology for remediating contaminated groundwater and water associated with natural gas treatment and production.

The specific research objectives were:

- To review the literature and data characterizing contaminated groundwater from the Strachan Gas Plant, to survey meteorological data from the region, and to identify water quality and atmospheric conditions for laboratory simulations.
- To estimate freeze-thaw process discharges and to evaluate regulatory requirements for the bench-scale demonstration and for a large-scale freeze crystallization water purification process.

- To conduct laboratory-scale process simulations for optimizing the design of the freeze-thaw process.
- To construct and shake down a 6-gal/hr (1200 lb/day) prototype unit to purify contaminated groundwater at the Strachan gas plant using artificial freezing technology.

All materials required for the artificial refrigeration prototype unit construction and assembly were purchased. The artificial refrigeration prototype unit was constructed. A block flow diagram illustrating the prototype unit construction is shown in Figure 3.

The preliminary operability testing of the prototype unit was conducted. The shakedown was initiated by first testing each individual process unit. During this time, process controls and monitors were calibrated and alarms tested. Process parameters such as centrifuge speed, groundwater feed rate, concentrate purge rate, wash water rate, and heat exchanger outlet temperature were investigated to obtain reasonable ranges of values for evaluation of the experimental prototype. To reduce costs, no chemical analyses were performed during the shakedown.

3.0 HYDROGEOLOGICAL SITE CHARACTERIZATION

Hydrogeological site characterization activities at Strachan involve monitoring the local groundwater regime and evaluating the seasonal changes that affect pumping at the site, as well as the effects of pumping itself. This effort is intended to provide a detailed characterization of the geologic materials that host, and thus interact with, the contaminants and the nature, occurrence, and flow of groundwater, which is the primary agent for contaminant movement at the site. Work on this task will also provide a monitoring network for the study of future aquifer behavior and for the assessment of future remediation research.

Activities in this area are designed to contribute to a comprehensive understanding of the Strachan site through refinement and expansion of the existing knowledge of the site. This is being accomplished, in part, through the evaluation of existing data using StratiFact®, version 4.0, a database-driven software package with graphical interface for the display and interpretation of aerial maps, stratigraphy, well construction, and analytical data. StratiFact® can illustrate spatially variable data, as well as temporally variable data, in a single display. These multidimensional data are typical for a transient groundwater flow regime, such as the one at the Strachan site, where pumping and injection affect the water levels and geochemistry on a daily basis.

Work during this phase involved familiarization with the site geology and hydrogeology and inspection of the existing groundwater monitoring network. Figure 4 provides a map of the Strachan Gas Plant site, along with locations of groundwater

Figure 3. RTC/UNDEERC freeze crystallization water purification process flow diagram.

Figure 4. Monitoring well location map at the Strachan Gas Plant.

monitoring and recovery wells. Figures 5 and 6 show stratigraphic sections at the site. The bedrock in the area is part of the Paskapoo Formation, a sedimentary unit typified by alternating layers of sandstone, siltstone, soft shales, and mudstone. Local observations indicate relatively flat-lying, or gently northwesterly dipping, fractured bedrock at an elevation of approximately 1200 meters (3940 feet) above sea level. Local bedrock topography includes a north-south-oriented bedrock surface depression (Figure 5), suggesting the presence of a major structural feature. The depression, identified by both coring and geophysical logging, is believed to be related to a major fracture zone. Overlying the bedrock are 6 to 12 meters of glaciofluvial sands and gravels, which are, in turn, overlain by 2 to 2.5 meters of sand and clay till.

The major hydrogeologic units at the site are the glaciofluvial sands and gravels and the bedrock. These units are in hydraulic connection. Within the fractured bedrock, the major groundwater-bearing zones are the sandstone layers and the weathered siltstones and shales. The groundwater surface elevation decreases from north to south, with the water table falling to within the bedrock south of MW4-A (Figure 6). On the average, the hydraulic conductivity in the overburden aquifer is 43 meters per day, corresponding to a linear groundwater velocity of one meter per day. Seasonal groundwater fluctuations of up to three meters have been observed at the site. These relatively large water-table elevation changes, as well as pumping efforts at the site, have resulted in the smearing of condensate across a significant section of the sands and gravels, resulting in much of the original contaminant volume becoming trapped in the unsaturated zone.

4.0 SUBSURFACE CONTAMINANT CHARACTERIZATION

The first step in accomplishing the goals of subsurface contaminant characterization is to establish a standard protocol and specify the techniques for sampling and analysis to be used during the program. The sampling and analysis protocol/techniques document was jointly developed through the efforts of the National Hydrology Research Institute (NHRI), Komex International, Inc., and the EERC. A copy of this document, entitled "Sour Gas Plant Remediation Research Project Quality Assurance/Quality Control Plan," is included in Appendix A.

The specified protocols and techniques are to be used by all project participants and laboratories to generate directly comparable data from the wide variety of project activities. The report not only specifies the protocols and techniques to be used, but also provides information on the sampling and analytical problems associated with the combined presence of the various contaminants.

Subsurface contaminant characterization studies performed at the EERC are designed to supplement the existing characterization data in order to better understand the nature and extent of the full range of contaminants present and gain additional insight into the potential interactions among contaminants, groundwater, and associated geological materials. Initial EERC activity involved the identification of organosulfur (thiophenes) and nitrogenous compounds (amines and amine degradation products) that are known to be present in the groundwater at the Strachan site, as well as selected inorganic constituents of interest that have not been previously identified, but are suspected to occur, including metals.

Figure 5. Subsurface stratigraphic profile at the Strachan Gas Plant (east-west section).

Figure 6. Subsurface stratigraphic profile at the Strachan Gas Plant (north-south section).

Table 2 lists the results of selected supplementary analyses performed on Strachan groundwater from recovery wells RW-8 and RW-13. Over 50 metals were scanned during a qualitative screening using inductively coupled argon plasma (ICAP) techniques. Those metals having detectable quantities in the Strachan groundwater, that are listed in the table, were all at concentrations less than current USEPA drinking water standards.

Samples of both RW-8 and RW-13 groundwaters and a sample of the natural gas condensate floating on the water table were subjected to gas chromatography/mass spectrometry (GC/MS) and gas chromatography/atomic emission detection (GC/AED) analyses.

TABLE 2
Results of Supplemental Characterization Analyses:
Strachan Gas Plant Groundwater

Constituent/Parameter	RW-8	RW-13
pH	6.9	6.9
Alkalinity (as CaCO ₃)	460	550
Hardness (as CaCO ₃)	465	465
Ammonia, mg/L	2.4	34
Nitrate, mg/L	<1	9.7
Nitrite, mg/L	<1	4.5
Total Kjeldahl Nitrogen (as N), mg/L	5.4	34
Phosphate, mg/L	<1	1.6
Sulfate, mg/L	<1	140
Chloride, mg/L	27	24
Barium, mg/L	0.6	0.3
Calcium, mg/L	140	140
Iron, mg/L	13	1
Magnesium, mg/L	28	28
Manganese, mg/L	2.5	0.8
Phosphorous, mg/L	0.06	0.3
Potassium, mg/L	0.9	2.9
Selenium, mg/L	<0.1	0.2
Sodium, mg/L	55	60
Strontium, mg/L	0.2	0.3
Sulfur, mg/L	12.8	116
Silicon, mg/L	3.1	4.1
Zinc, mg/L	0.4	<0.003
Total Inorganic Carbon, mg/L	130	120
Total Organic Carbon, mg/L	40	55
Chemical Oxygen Demand, mg/L	110	73
Total Dissolved Solids, mg/L	710	760
Conductivity (mmho/cm)	0.9	0.7

All GC/MS identifications were tentative, based only on mass spectra. Identifications of common species such as alkyl benzenes, phenols, indole, alkanes, and elemental sulfur (S_8) are very certain. The identification of other species (mostly cyclic alkanes) are more tentative, but are fairly certain to be the correct compound class and molecular weight.

The condensate sample, collected from RW-13, appeared to have been depleted of species on the more water-soluble end, such as benzene and toluene, and contained, in decreasing order by concentration, C2- to C5-alkyl benzenes (mostly C2- and C3-), C6- to C22-n-alkanes (mostly C7 with lesser amounts as the molecular weight increased) and smaller amounts of related branch alkanes, C6- to C9-cyclic alkanes (mostly C7 and C8), and elemental sulfur.

GC/AED analysis demonstrated that the condensate sample did not contain significant nitrogen-containing organics but did have sulfur-containing organics. The sample exhibited a large elemental sulfur peak as well as approximately 30 more volatile sulfur-containing organics. While the chromatographic behavior was consistent with alkyl thiophenes, alkyl benzothiophenes, and alkyl dibenzothiophenes, the concentration of the sulfur-organics was too low to allow GC/MS identification without significant additional effort.

The groundwater samples were extracted with methylene chloride after pH adjustment to 12 to obtain the base/neutral fraction and again after pH adjustment to 2 to obtain the acid fraction. The extracts were then evaporated to 100 μ L for analysis.

Essentially all of the organics extracted from the groundwaters were in the base/neutral fraction and none of the more obvious acids, such as phenol, were detected by GC/MS. As would be expected, the organics in the water reflected the organics in the natural gas condensates. RW-8 groundwater contained mostly C2- and C3-alkyl benzenes and much lesser amounts of n-alkanes. RW-13 groundwater contained mostly C2- and C3-alkyl benzenes, lesser amounts of n-alkanes and branched alkanes, and elemental sulfur. A third groundwater sample, collected from RW-12, contained toluene, C2- and C3-alkyl benzenes, elemental sulfur, and naphthalene and C1-naphthalenes.

GC/AED analyses of the groundwater extracts for sulfur-containing species yielded similar results to those obtained for the condensates. RW-8 contained about 30 significant S-containing organics, mostly in the more volatile BTEX range, as well as a lesser amount of elemental sulfur. RW-13 also showed several sulfur-containing organics, but the pattern was dominated by species less volatile than those found in RW-8 and a very large elemental sulfur peak.

A sample of the black material from RW-13 (see Section 2.1) was collected from the oil/water separator used in the existing pump-and-treat system. Preliminary observations showed that the material was readily oxidized upon exposure to the atmosphere, turning from black to brown in color. A bulk sample of the black material was subsequently dried under a nitrogen atmosphere to prevent oxidation prior to analysis. When dried under a nitrogen atmosphere, the material remained black. A sample of the dried material was subjected to an ultimate analysis for the determination of hydrogen, carbon, nitrogen, and sulfur content. The results of the ultimate analysis showed the material to contain

approximately 2% hydrogen, 9% carbon, 2% nitrogen, and 34% sulfur, with an ash content of 57.5%.

The material was also analyzed for iron, sulfur, and manganese using inductively coupled argon plasma/atomic emission spectroscopy (ICAP/AES). Results of this analysis indicated an iron content of 36%, a sulfur content of 35%, and a manganese content of 0.08%.

The sample was then subjected to analysis by scanning electron microscopy (SEM) microprobe analysis. Results of the SEM analysis are shown in Table 3. SEM analysis showed the material to be predominantly composed of iron and sulfur, corresponding to the results of bulk analyses. SEM analysis also showed the material to be clusters of very small particles, less than one micron in size, but it could not be determined if the particles were of crystalline structure.

The dried black material was also analyzed using gas chromatography with atomic emission detection (GC/AED). The material was sonicated using benzene for approximately one hour prior to analysis by GC/AED. Results of this analysis showed the material to be composed primarily of n-alkanes in the C7- to C17- range, with approximately 5% elemental sulfur.

Based on the results of the analyses described above, it appears that the material is an iron sulfide precipitate, likely containing some iron oxyhydroxides. The material is extremely finely divided with individual particles less than one micron in size, possibly accounting for the high reactivity of the material when exposed to air.

TABLE 3

Results of SEM Analysis of Black Material from RW-13:
Strachan Gas Plant Groundwater

Element	Weight Percent
Sodium	0.00
Magnesium	0.19
Aluminum	0.00
Silicon	0.12
Phosphorous	0.18
Sulfur	35.79
Chlorine	0.00
Potassium	0.09
Calcium	1.23
Titanium	0.00
Chromium	0.00
Iron	41.69
Barium	0.00
Oxygen	5.73
Total	85.02

5.0 SOIL VAPOR EXTRACTION

Preliminary research has shown SVE to be a suitable remediation technique for volatile organic contaminants (VOCs) in the subsurface at the Strachan Gas Plant. SVE involves the application of a vacuum at an extraction well to induce air and gaseous-phase contaminants in the unsaturated zone to advect toward the extraction well where they are removed from the subsurface. As clean air replaces the contaminated air in the subsurface, the remaining VOCs are volatilized as the system attempts to restore chemical equilibrium in the soil pores. In this manner, the continued application of SVE is often able to remove a majority of the volatile contaminants in the unsaturated zone.

During this phase of SVE research, an easily accessible site at Strachan was selected that had high levels of subsurface contamination, and a prepilot vacuum test was performed. Geologic and hydraulic characterizations were conducted, making use of borehole logs and geophysical methods to determine stratigraphic boundaries and identify layers with varying permeability. Column tests were performed to characterize anticipated temporal changes in offgas concentration and composition and to estimate the practical limits of condensate removal.

The prepilot vacuum test was conducted at the selected Strachan site to provide an initial indication of the degree to which air is able to flow through the subsurface under an applied vacuum. The test indicated that the sands and gravels at the site are very permeable to air and essentially isotopic, with an effective radius of influence of approximately 15 meters. Preliminary vapor surveys indicated a wide range of soil vapor concentrations. Detailed vapor composition is currently being determined using gas chromatography.

Computer modeling, the primary emphasis of EERC activities, is an important factor in the SVE efforts. Modeling efforts were focused primarily on the application and verification of computer models that attempt to simulate the transport and fate of the organic compounds in the unsaturated zone. Once verified, the model(s) will assist in the actual design of the SVE remediation system, providing input as to the size and number of extraction wells required, their spacing, and location and duration of operation. The three main factors controlling the performance of SVE operations that must be addressed in the model include the chemical composition of the contaminant, the vapor flow rate through the unsaturated zone, and the flow path relative to the location of the contaminant.

Two types of models were used to simulate SVE operation at Strachan. First, simple analytical models were applied to obtain estimates of subsurface air conductivity, radius of influence, and steady-state pressure distribution. The two models applied at this level were AIRTEST (USGS) and GASWELL (by Gary A. Robbins).

The second and more complex models that were identified as having potential application included SV2DV (by Klaus M. Rathfelder, presently at the University of Michigan), an unnamed model (Southern Illinois University), VENTING (Environmental Systems & Technologies, Inc.), and AIRFLOW, a modified version of the groundwater flow model MODFLOW (USGS).

Information for estimating plume position from travel times and predicting rates of removal over time is best handled by two- and three-dimensional flow and transport models. Since some three-dimensional information is available from multilevel well installations and electromagnetic borehole logs, the focus shifted to a more elaborate soil SVE model, SV2DV in particular.

The SVE operation at Strachan was simulated with SV2DV (soil vapor, 2-dimensional flow, vertical configuration), a numerical finite difference model. This model was written by Klaus M. Rathfelder and was made available courtesy of the author. The mathematical representation of soil vapor extraction processes was formulated for a multicomponent, multiphase, heterogeneous, porous medium. Principal assumptions of the model are isothermal conditions, immobile liquid phases, and negligible chemical and biological transformations at the time scale of simulated SVE runs.

From preliminary chemical characterization of Strachan SVE offgases, the compounds with dominant presence have been identified: pentane, methylpentane, hexane, methylcyclopentane, cyclohexane, methylheptane, methylcyclohexane, toluene, octane, and *o*-, *m*-, *p*-xylenes. Although SV2DV is a multicomponent model with up to six compounds, computer simulations become very time-consuming when more than three compounds are modeled. Therefore, only three chemicals from the above list have been chosen, based on their abundance in the offgases, and on their chemical properties. The chemical properties required by the model are molecular weight, liquid density, vapor pressure, water solubility, Henry's law constant, vapor viscosity, and binary diffusion coefficient. To maximize the range of these properties in the model, the following three compounds have been chosen: 1) methylcyclohexane (highest in concentration), 2) methylpentane (highest in vapor pressure and Henry's Law constant, lowest in solubility) and 3) *o*-xylene (lowest in vapor pressure and Henry's Law constant, highest in solubility).

Simulation runs with SV2DV have first been calibrated with observed pressure data measured at, and around, extraction well SVE-1. Figure 7 shows the pressure distribution with radial distance between the measuring point and SVE-1. Ideally, the relationship should show a hyperbolic drop with increasing distance, but soil heterogeneities, well losses, and leaks in the confining layers (natural, or due to drilling) and/or leaks in the plumbing disturb the ideal pattern. The best fit of observed versus modeled pressures was obtained for an aquifer consisting of two layers, the lower one with an air permeability 100 darcy (the intrinsic permeability of 10^{-12} m² equals 1 darcy). SV2DV simulation of this scenario is shown in Figure 8. The data in Figure 8 correspond with measured data in Figure 7, both near the extraction well, located on the left side of the illustration, as well as far from the well (at 35 m from SVE-1, both Figures 7 and 8 show a corresponding suction of 0.5 inches of water). After the model has been calibrated for the physical scenario (pressure distribution), the chemical runs were conducted for soil air concentrations of the three selected hydrocarbons.

In order to calculate the chemical proportioning of a chemical between the liquid, solid and vapor phases, an initial distribution of the chemical in the subsurface must be known. Because this initial, or starting, condition has not been determined prior to SVE, only rough guesses on the state of the Strachan condensate at the onset of the SVE operation can be made. The initial guesses include the following: simplified condensate composition by mole-fraction is methylcyclohexane 0.50, methylpentane 0.25, *o*-xylene 0.25. Initial concentration of condensate in the pores on volume basis is 1% (this is

Figure 7. Observed pressure distribution.

presumed to be the concentration in the "smearing zone," not the residual concentration), and the contaminated area is from 5.0 to 7.5 meters below ground level, extending 14 meters from SVE-1 in all directions. Soil moisture concentration is assumed to be 15% by volume.

Figures 9, 10, and 11 show the simulated soil air concentration in parts per million (ppm) for methylcyclohexane, methylpentane, and *o*-xylene at approximate time intervals of 2.5, 22.5, and 80 minutes from the onset of the blower at SVE-1. The extraction well operates at 680 ft³/min and is screened from 2 to 5 meters above the water table. After 80 minutes, virtually all the contaminated soil air has been evacuated. Minor differences can be observed at this time in the behavior of the three compounds as "hanging above the screen." The most pronounced is for *o*-xylene, which has the highest tendency to dissolve in soil moisture.

Cumulative concentration plots indicate that 10% (by mass) of the total condensate has been removed after 80 minutes because of extraction of the soil air. Further extraction, however, showed the well to be yielding such low concentrations that the computer code had difficulty in distinguishing them from zero. Concentrations in the liquid phase and in the solid phase remained, therefore, unchanged. The problem with this response should be sought in the choice of the initial and boundary conditions. It is becoming evident that the condensate vapor is being drawn from farther than a radius of 14 meters from the extraction well, as was indicated by a prepilot soil vacuum test. Also, the initial amount of condensate in the contaminated zone may be more than 1% and possibly more than the residual concentration, with the implication that liquid condensate would be mobile. The process of lateral inflow and outflow of condensate is not considered by this model.

Figure 8. Simulated pressure distribution.

Figure 9. Concentrations (ppm) of methylcyclohexane in a vertical profile with the pumping well along the left border. Dimensions are in meters.

Figure 10. Concentrations (ppm) of methylopentane in a vertical profile with the pumping well along the left border. Dimensions are in meters.

Figure 11. Concentrations (ppm) of o-xylene in a vertical profile with the pumping well along the left border. Dimensions are in meters.

APPENDIX A

SOUR GAS PLANT REMEDIATION TECHNOLOGY RESEARCH AND DEMONSTRATION PROJECT: QUALITY ASSURANCE/QUALITY CONTROL PLAN

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SOUR GAS PLANT REMEDIATION TECHNOLOGY RESEARCH AND DEMONSTRATION PROJECT QUALITY ASSURANCE/QUALITY CONTROL PLAN

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 "CAPP Sour Gas Plant Remediation Project: Quality Assurance/Quality Control Plan." 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 sampling and analyses of the subsurface contaminants 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 QA/QC for this project will emulate that of the U.S. Environmental Protection Agency's (EPA) Contaminated Soil and Debris (CSD) plan.

2.0 PROJECT DESCRIPTION

The purpose of this project is to develop a sampling and analysis protocol for the assessment of subsurface contamination as a result of sour gas treatment plant operations. The participating research groups will be responsible for conducting field and analytical procedures in such a manner as to maintain consistency in the data collected and to validate the results of the analytical procedures.

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 1 shows project authority lines.

The CAPP subsurface investigation is managed by a task force composed of the following key personnel:

- Project Directors
- Project Manager
- QA/QC Team Leader
- Analytical Team Leader
- Health and Safety Officer

Figure 1. Task force organizational chart.

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 the following:

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

The project manager is also responsible for:

- Ensuring that data are collected, analyzed, reported, and stored in a manner consistent with the quality policy.
- Designing the field investigation, including sampling points.
- 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.

3.3 QA/QC Team Leader

Responsibilities of the QA/QC team leader include the following:

- Generation and promulgation of the QA/QC project plan

- Scheduling, planning, and conducting quality reviews; issuing reports; retaining records; and following up on corrective actions

3.4 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 site-specific standards. Other duties will include the following:

- 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 inspections
- 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

3.5 Analytical Coordinator

Responsibilities of the analytical coordinator include the following:

- Collaborating with the project manager and the QA/QC team leader in establishing sampling and testing programs
- Serving as the collection point for reporting of nonconformances and changes in laboratory activities
- Serving as a liaison between the project management and laboratory personnel
- Notifying the laboratory and project management 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 project's sampling and analysis efforts: to produce well-documented, quality data that can be used to determine the best treatment standards and technologies for the subsurface contamination. The types of data that will be produced fall into two distinct categories: characterization data and treatment data.

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

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

The quality of the analytical data for this project will be assessed 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 samples and each treatment residual sample following the test methods given in SW-846 (USEPA, 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 laboratory will try to achieve the lowest detection limit possible for all constituents of interest.

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 matrix spike duplicate, where applicable. Precision is calculated using the following equation:

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

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 samples collected during the characterization visits, matrix spikes will be completed. For the treatment test analysis, a matrix spike and a spike duplicate will be completed on one sample from the untreated samples and one sample of each type of 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:

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

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).

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

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 concentration levels 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 nondetection 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 activities initiated that are actually finished. 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 completeness is less than 100%, documentation will be provided 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 will be removed from the samples, if possible.

4.5 Comparability

Comparability for each treatment test will be addressed through the use of identical analytical procedures. The analytical data will be reported in the same units for each test for all samples collected.

5.0 COLLECTION PLAN FOR SAMPLES

The purpose of this sampling and analysis program is to determine the level and extent of groundwater and soil contamination at the Gulf Strachan site. Individual sampling and analysis plans for each environmental medium will be prepared and will include the following information:

- 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

Any samples obtained during the course of the field investigation will be collected in a manner which ensures that they are representative of the site and free of contaminants from sources other than the immediate environment being sampled. The equipment and the techniques that will be employed to obtain representative, unbiased samples will be in accordance with EPA-recommended procedures. Appendix A provides general sampling procedure guidelines for volatile organic compounds, semi-volatile organic compounds, and inorganic compounds. Appendix B provides the protocol for sampling of monitoring wells.

5.1 Sampling Procedures for Characterization Samples

At least one sample from each medium will be collected, in duplicate, during each site characterization visit. The sample will be collected from the location with the greatest contamination concentrations that meet the objectives of the treatment test to be conducted. Final selection of locations to be sampled will be determined by the project manager. The existing data used to select the locations will be presented in the SAP.

The procedures used to collect the samples will vary depending on the sampling location. The equipment that will be used to collect the samples must be specified in the SAP. For sites contaminated with volatile organics, equipment such as a photoionizer, organic vapor analyzer, or a combustible gas indicator should be used to determine the location with the highest concentrations.

Each characterization sample of untreated soils should be a composite of six subsamples. All debris in the subsamples should be removed. The subsamples must be broken up with a spatula and mixed/blended prior to compositing. The sample aliquots for each analytical test to be conducted will then be taken from the composited material. The characterization SAP must document how the samples are to be collected and composited. The final characterization report must document the location from where the subsamples were collected and any deviations or modifications from the SAP that were required to take the samples.

A matrix spike sample will be analyzed for the characterization samples to assess whether the sample matrix presents any analytical problems that will affect obtaining adequate spike recovery values from the samples taken during the actual treatment test. The matrix spike will be prepared in the laboratory. The constituents to be spiked and the concentration levels for the spiked constituents must be specified in the SAP.

5.2 Sampling Procedures for Treatment Tests

Prior to treatment testing, the soil and groundwater to be treated must be excavated and pumped, respectively, unless treatment is to be performed in situ. The treatment test SAP must discuss these activities and should identify the affected areas on a topographical map. This area should be the same location from which the site characterization sample was taken. In addition, the quantity of soil and groundwater required for the treatment test must be specified in the SAP.

The treatment test SAP must document any decontamination procedures that will be required for the excavation and pumping equipment. In addition, the SAP must discuss how decontamination water and any contaminated disposable sampling equipment will be disposed of after the treatment test has been completed.

If the soil or groundwater requires preparation (such as grinding or blending of the soil or filtering of the water) prior to being treated, the SAP should discuss what procedures may be used, and an on-site engineering report (OER) should document the exact procedures that were used. The untreated samples for the test should be collected after this preparation step.

Sampling procedures, locations, and frequencies must be documented in the treatment test SAP. Sampling times for the untreated and treated samples must take into account the residence time of the treatment system. The untreated and treated samples must be corresponding matched pairs so that waste characteristics can be evaluated and a material balance can be completed. Any deviation from obtaining matched pairs must be documented in the SAP and must be approved by the project manager. If possible, six sets of untreated and treated samples will be collected. However, the final selection of the number of sampling sets needed to evaluate the treatment system must be approved by the project manager and presented 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 subsamples. The soil subsamples must be broken up with a spatula and mixed/blended prior to compositing.

The sample aliquots for each analytical test to be conducted will then be taken from the composited material. The site-specific SAP must document how the subsamples are to be collected and composited. The OER must document the location from which the subsamples were collected and any deviations or modifications from the SAP that were required to collect the samples.

A spike and a spike duplicate analysis must be completed for the untreated soils and groundwater and the treatment residuals. These spikes will be prepared in the laboratory. The sample set to be spiked, the constituents to be spiked, and 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. These data will be used to evaluate the performance of the treatment system. 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 Sampling Documentation

All sampling activities will be documented through the use of field logbooks, sample analysis request forms, and field log sheets. Documentation will include, but will not be limited to, the following:

- Well purging data
- Field measurement data and sample characteristics
- Field equipment used
- Sampling location and depth
- Sampling order
- Sample containers used
- Documentation procedures
- Sample preparation and preservation procedures
- Reagents, filtering techniques, etc.
- Calibration methods and frequency for field devices
- Collection of replicate samples
- Ancillary data: weather conditions (cloud cover, wind speed and direction, precipitation occurrence, temperature, etc.) and ground conditions (standing water, frozen soil, etc.)

5.4 Equipment Handling and Decontamination Procedures

All materials and equipment that will come in contact with the sample or be inserted into the well bore will be cleaned prior to obtaining each sample to avoid cross-contamination of wells and to assure representative samples.

Care will be taken to prevent materials contamination through handling and storage. Equipment (water level probes, pH and conductivity probes, funnels, etc.) will be decontaminated and placed in new plastic bags between measurements. Disposable gloves will be worn at all times, and no contact between exposed skin and the sample containers or sampling equipment will be allowed. Gloves will be discarded after each sampling event and before and after each decontamination procedure. A plastic sheet will be used to avoid contamination of equipment temporarily placed on a surface. This plastic sheet will also be discarded after each sampling and before each decontamination event. All

containment bags, plastic sheets, disposable gloves, and rope will be placed in plastic garbage bags when discarded and then disposed of in an acceptable manner.

In addition to the above procedure for dealing with sampling equipment, all work will be performed in accordance with standard safety procedures. Rubber boots and safety goggles will be worn during all sampling activities.

5.5 Field QA/QC Activities

5.5.1 Representativeness

Sampling locations will be chosen so that they are representative of the untreated soil, groundwater, and 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. The subsamples from field composites will be mixed thoroughly before sending the sample aliquots are sent to the laboratory.

5.5.2 Backup Samples

A backup sample aliquot will be collected to ensure the 100 percent completeness data QA/QC objective. Backup samples 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.

5.5.3 Containers

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

5.5.4 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 whether the glassware or other field equipment was a source of contamination. One equipment blank per site visit per type of equipment to be decontaminated or per decontamination procedure to be used will be collected if field equipment is to be decontaminated and reused. At a minimum, one equipment blank per sampling episode for a treatment test must be collected and analyzed even if all field equipment is new. If field decontamination procedures are to be used, they must be documented in the characterization and/or treatment test SAP. The number of equipment blanks to be analyzed and the parameters for which they are to be analyzed must be specified in the site-specific SAP.

Trip Blanks. Trip blanks are used to determine whether any contamination resulted from sample transport, shipping, or site conditions. One trip blank that is not opened in the field will be taken. The parameters for which the trip blank is to be analyzed must be specified in the SAP. The trip blank will be prepared by pouring laboratory-pure water into the sample container. The blanks 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 free of contaminants that may interfere with analytical tests.)

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. 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.

5.6 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 SAP provides information concerning the containers, sample sizes, holding times, and sample preservation requirements for various analytical parameters used in analyses of organic and inorganic compounds.

5.7 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.

- 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 samples are homogenized, composited, and split. The aliquots are then transferred to the appropriate sample containers. For grab samples, a sufficient sample is taken, mixed, and transferred to the appropriate sample containers.
- Observations and judgments about sample homogeneity and the fact that split samples were provided are recorded in the field logbook.

5.8 Sample Collection

The SAPs will contain sample collection protocols that address the following considerations:

- **Sampling Point Descriptions.** The sampling points selected and the justification for their selection must be provided. All 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 characterization samples, the composite will be composed of six subsamples. For treatment tests, composite samples of the untreated soil, groundwater, and treatment residuals will be composed of three subsamples. In addition, the logistics of excavation and transport of the contaminated soil and groundwater will be documented.
- **Frequency.** The frequency of sample collection at each sampling location will be specified in the SAP and selected to best characterize the variability in the 1) soil and groundwater samples, 2) treatment processes, and 3) analytical results. If possible, for the treatment tests, 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 systems. The untreated and treated samples are to be corresponding matched pairs.
- **Constituents to Be Analyzed.** All analyses will be performed using SW-846 methods, other EPA-approved methods, or specific methods as listed in this document.
- **Total Composition and TCLP Extracts.** All samples will be analyzed for total composition of inorganic constituents. Table 1 lists the heavy metals that are regulated under the toxicity characteristics rule and the action levels.
- **Sample Containerization and Preservation.** Procedures for sample containerization and preservation will be documented. A sufficient amount of sample will be collected to complete each analysis requested. In addition, for the sample set for which a matrix spike and a matrix spike duplicate are to be analyzed, a sufficient amount of sample must also be collected for these additional analyses.

TABLE 1

Heavy Metal Constituents Regulated Under the Toxicity Characteristics Rule

Constituent	Hazardous Waste Code	Regulatory Level in TCLP Extracts, mg/L
Arsenic	D004	5.0
Barium	D005	100.0
Cadmium	D006	1.0
Chromium	D007	5.0
Lead	D008	5.0
Mercury	D009	0.2
Selenium	D010	1.0
Silver	D011	5.0

- **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 will be specified in the SAP.

5.9 Health and Safety Plan

The sampling team will follow health and safety protocols established for each site. At a minimum, the health and safety plan 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 2) 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 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.

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

Figure 2. Example of chain-of-custody record.

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 samples 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 terminate upon laboratory receipt of samples.

6.2 Sample Transport

Samples will be packaged and labeled for shipment in compliance with current Canadian and 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 hazardous waste 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, if collected, 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 a separate plastic bag to prevent cross-contamination if breakage occurs.

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 or 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, i.e., one shipment form for each 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 be delivered to the laboratory either 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. 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 sample 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, access to which will be limited to laboratory employees.

7.0 ANALYTICAL PROCEDURES

Analytical methods performed by the participating research groups should be as indicated in Table 2 where possible or selected from EPA Office of Solid Waste-approved methods, most of which appear in "Test Methods for Evaluating Solid Waste" (USEPA, 1986). These methods are those specified by the EPA, federal and state agencies, and professional organizations. It is recommended that the laboratory obtain the following documents prior to conducting analyses for this project:

- Guidelines establishing test procedures for the analysis of pollutants under the Clean Water Act, 40 CFR (Code of Federal Regulations), part 136
- Hazardous waste management, 40 CFR, parts 260-265, 268, and 280
- U.S. Environmental Protection Agency (USEPA), 1986, "Test Methods for Evaluating Solid Waste"
- American Public Health Association, American Water Works Association, and Water Pollution Control Federation (APHA, AWWA, and WPCF), 1985, "Standard Methods for the Examination of Water and Wastewater"
- U.S. Environmental Protection Agency, Contract Laboratory Program (CLP) protocols for the analysis of organic and inorganic hazardous substances
- Annual book of ASTM standards, 1987, v. 11.01, 11.02, and 11.04

The analytical laboratory must have available for review documentation of all methods used routinely in the form of an SOP. The SOP must contain detailed instructions concerning the use of the method. Any deviation from published methodology is documented and explained in the SOP.

Before an analytical method is used for this project, the laboratory must provide documentation to demonstrate that the method was validated. Validation criteria consist of the following:

- 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 methods for organic and inorganic parameters that may be analyzed for in characterization and treatment test samples. All SAPs must specify the exact analytical methods to be employed.

TABLE 2

Recommended Methods for Inorganic and Organic Analyses

Parameter	Preparation Method ^a	Analysis Method ^a
Inorganic Constituents		
Soils, Solids, and Sediments		
Metals, total		
Inductively Coupled Plasma (ICP) Metals	3050	6010
Arsenic	3050	7060
Chromium (hexavalent)	1311	7197
Lead	3050	7421
Mercury		7470
Selenium	3050	7740
Thallium	3050	7841
Metals, TCLP	1311 followed by:	
ICP metals	3010	6010
Arsenic		7060
Chromium (hexavalent)		7197
Lead	3020	7421
Mercury		7470
Selenium		7740
Thallium	3020	7841
Cyanides		9012
Fluorides		MCAWW ^b 340.2
Sulfides		9030
Ash Content		ASTM D3174
Ash Fusibility		ASTM D1857
Cation Exchange Capacity		9080/9081
Chemical Oxygen Demand		MCAWW 410.1-.4
Chloride		9250
Clay Content		X-ray diffraction
Corrosivity		1110
Heating Value		ASTM D2015

TABLE 2 (continued)

Parameter	Preparation Method ^a	Analysis Method ^a
Moisture Content		ASTM D2216
Nitrogen Content		ASTM E148
Oil and Grease		9071
Redox Potential of Leachate		ASTM D1498
Permeability ^c	ASTM D698	9100
Pore Volume		ASTM D4404
pH		9045
Phosphorous Content		MCAWW 365.4
Specific Gravity		ASTM D854
Sulfate		9036
Sulfur Content		ASTM D4239
Surfactant Concentration		MCAWW 425.1
Total Halogens		ASTM D808
Total Kjeldahl Nitrogen		ASTM D3179
Total Organic Carbon		Lloyd Kahn
Total Organic Halides		9020
Waters		
Metals		
ICP Metals	3010	6010
Arsenic		7060
Chromium (hexavalent)		7197
Lead	3020	7421
Mercury		7470
Selenium		7740
Thallium	3020	7841
Cyanides		9012
Fluorides		MCAWW 340.2
Sulfides		9030
Acidity		MCAWW 305.1
Alkalinity		MCAWW 310.1

TABLE 2 (continued)

Parameter	Preparation Method ^a	Analysis Method ^a
Bromide		MCAWW 320.1
Chemical Oxygen Demand		MCAWW 410.1-.4
Chloride		9250-52
Color		MCAWW 110.1-.3
Conductance		MCAWW 120.1
Corrosivity		1110
Hardness, total		MCAWW 130.1-.2
Heat Value		ASTM E711
Iodide		MCAWW 345.1
Nitrogen		
Ammonia		MCAWW 350.1-.3
Kjeldahl, total		MCAWW 351.1-.4
Nitrate		MCAWW 352.1
Nitrate-Nitrite		MCAWW 353.1-.3
Nitrite		MCAWW 354.1
Odor		MCAWW 140.1
Oil and Grease		9070
Redox Potential		ASTM D1498
pH		9040
Phosphorus		MCAWW 365.1-.4
Solids		
Filterable		MCAWW 160.1
Nonfilterable		MCAWW 160.2
Total		MCAWW 160.3
Volatile		MCAWW 160.4
Settleable Matter		MCAWW 160.5
Specific Gravity		ASTM D891
Sulfate		9035/9036/9038
Total Organic Carbon		9060
Total Organic Halides		9020/9022

TABLE 2 (continued)

Parameter	Preparation Method ^a	Analysis Method ^a
Turbidity		MCAWW 180.1
Viscosity		ASTM D445
Organic Constituents^d		
Total Petroleum Hydrocarbons	Freon extraction with infrared detection (USEPA, 1990)	
C ₁₋₄ Hydrocarbons	Dissolved gases displaced under vacuum with gas chromatography (GC) thermal conductivity detection (ASTM, 1979)	
C ₅₋₃₀ Hydrocarbons (USEPA, 1990)	Solvent extraction with GC-FID	
Total Purgeables	Dynamic headspace or purge and trap gas chromatography-mass spectroscopy (GC-MS) (USEPA, 1990); dynamic headspace or purge and trap GC-FID (USEPA, 1990)	
BTEX (benzene, toluene, ethylbenzene, and xylene)	Dynamic headspace or purge and trap GC-MS (USEPA, 1990); dynamic headspace or purge and trap GC-FID (USEPA, 1990); static headspace GC-FID (Roe, 1989; MOE, 1990)	
Volatile Priority Pollutants	Dynamic headspace or purge and trap GC-MS (USEPA, 1984a)	
Polynuclear Aromatic Hydrocarbons	Methylene chloride extraction with GC-MS (USEPA, 1984b)	
Amine Degradation Products	Solvent extraction, GC-FID; GC-MS; GC-AED	
Organosulfur Compounds	Open scan VOA; open scan semivolatiles GC-AED	

^a All methods are SW-846 methods unless otherwise specified.

^b Methods for chemical analysis of water and wastes (USEPA, 1981).

^c Permeability is done usually at 90% of standard proctor. Documentation for the percent of standard proctor used for the analysis must be provided with the data.

^d Methods for petroleum contaminants, process chemicals, and amine degradation products in groundwater.

For all samples analyzed, the laboratory must provide documentation concerning the methods used for the constituent parameter of interest and any modifications or deviations required to analyze the various samples. The methods used will be documented in all characterization reports and OERs.

8.0 QA/QC PROCEDURES

The overall effectiveness 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 CORRECTIVE ACTION

This section describes procedures and responsibilities for accomplishing corrective action and for providing timely information to management regarding the effectiveness of activities affecting the QA/QC project.

9.1 Procedure

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

9.2 Corrective Action

The need for corrective action may be identified during the review of data, field investigation, field and office surveillance, 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 review 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.

9.2.1 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 plausible corrective action. The effects of the action will be tested to determine whether the action eliminates the problem and associated concerns.

After the success of the corrective action has proven to be likely, the project manager, QA/QC team leader, or their designees are responsible for documenting and implementing all corrective actions. They will write a Corrective Action Memorandum that documents the problem and then 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.

9.2.2 Data Outside Control Limits

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

- If a field and/or laboratory person observes that instruments are not within calibration limits, then the instruments will be recalibrated; samples will be reanalyzed once an acceptable calibration has been obtained.
- If the field and/or laboratory person or engineering staff observes data problems (for example, if results for specific QA/QC analysis are outside the QA/QC limits), then that person will immediately notify the contractor 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 as follows:
 - ***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 do not affect validity of the data; i.e., detection limits for a few of the analytes were between 1 and 2 ppm, and the project manager was not contacted. A problem memorandum will be prepared and sent to the project manager; 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.

9.2.3 Data Problems

The project manager will investigate the problem and will be responsible for ensuring that one or more of the following actions are 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.

9.2.4 Unusual Occurrences and Unexpected Events

During a field investigation, there is a limit to the predictability of field conditions. If a condition is encountered that is totally outside of, or contrary to, those 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) will be immediately contacted and their direction obtained for the completion of activities. Any such deviation from field planning and procedures will be documented in field notebooks and an action memo prepared. Action memos will be prepared by the responsible engineer and processed by the QA/QC team leader. The causes and actions to prevent recurrence of the deviation will be determined and concurred with by the project manager and the QA/QC team leader. The QA/QC team leader will track the action memo and be responsible to document resolution of the deviation.

9.2.5 Management Corrective Action and Stop Work

Quality deficiencies serious enough to warrant management action will be identified and reported in a management corrective action report (MCAR). Conditions requiring management corrective action may be identified by anyone associated with a project. Such conditions will be reported to the QA/QC team leader by preparation of a MCAR form. The MCAR will identify 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.

9.2.6 Laboratory Internal Corrective Action

When errors, deficiencies, or out-of-control situations exist, the QA/QC project provides systematic procedures called "corrective actions" to resolve problems and restore proper functioning to the analytical system.

Corrective actions may be necessary if the following occur.

- 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 reviews, 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.

10.0 CALIBRATION PROCEDURES

10.1 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 an 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 and/or 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 solution. If the standards are made from pure standard materials, the

materials must be assayed and the purity of the standard must be known. 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.

10.2 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. In addition, calibration checks will be made by the crew chief at times specified in the SAP.

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.

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

10.3 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.

10.4 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.

TABLE 3

Calibration Procedures for Analytical Instruments

Instrument	Procedure
Flame Atomic Absorption (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- μ g/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.
High-Performance Liquid Chromatography (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.
Total Organic Carbon Analyzer (TOC)	Daily single-point calibration in triplicate. Check standard every 20 samples.
Total Organic Halides Analyzer (TOX)	Daily calibration check. Check standard every 20 samples.
Ion Chromatography (IC)	Daily multipoint calibration. Check standard every 20 samples.
Thermometers	Check against National Bureau of Standards thermometer every 6 months.

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

11.0 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. Following review by the supervisor, the data package must be reviewed by the QA/QC team leader.

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

11.1 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, reducing 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 line-out, and adding the revised information next to the line-out.

11.2 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 or the data reduction staff 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 or the data reduction staff to verify that all instrument systems are in control and that QA/QC objectives for precision, accuracy, completeness, and method detection limits are being met.

The principal criteria that will be used to validate the integrity of data during collection and reporting are as follows:

- Verification, on a weekly basis, by the project analyst, that all raw data generated in the preceding week have been stored on magnetic tape 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 data 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, 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 QA/QC team leader and project manager. If the data must be reanalyzed and reanalysis corrects the problem, then only the reanalysis results will be reported. If both initial analysis and reanalysis results indicate a matrix problem, 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.

11.3 Reporting

A variety of reporting formats may be used. In general, reports will consist of a copy of the sample log sheet, 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 in 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 (including the expected value, percent recovery, control limits, lot number, and source where appropriate) of any matrix spikes, duplicates, matrix spike 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 $\mu\text{g/L}$ 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 package.

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.

12.0 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.

12.1 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 taken on the sampling trip. Following the field equipment's use, it must be decontaminated using the appropriate cleaning procedures required for the project.

12.2 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, mercury thermometers, and electronic 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. Some of these items include 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.

13.0 QA/QC REPORTS TO MANAGEMENT

The project manager, in conjunction with the QA/QC team leader, will identify critical areas of the project that may 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 work group members may request 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, 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 sampling and analysis plans.

Reports for this project, 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 inspections
- Assessments of data quality in terms of precision, accuracy, completeness, method detection limit, representativeness, and comparability

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ATTACHMENT A-1

**GENERAL DETAILS FOR ORGANIC AND
INORGANIC SAMPLING PROCEDURES**

APPENDIX

General Details on Sampling Procedures for Volatile Organic Compounds

Collect triplicate samples for all sample sites.

40 mL vials are supplied precleaned to QA/QC specifications.

For samples requiring preservation, add 3-4 drops of conc. HCL to vial in the laboratory prior to field trip. The HCL is a preservative to slow down biodegradation.

If free chlorine is suspected at sample locations (not expected at natural-gas plants but common for eg: Swimming pools, water treatment plants) granules of sodium thiosulphate are added to the vials first and HCL is added in the field to vials filled with the water samples.

Secure the septum cap to finger tightness, avoiding contact with the teflon cap.

For a batch survey prepare a field blank by filling a 40 mL vial, containing the HCL preservative, with organic free water. Make sure that there is no headspace.

Avoid aeration during sampling and undue exposure of the sample vials to organic contamination from car exhaust fumes, solvents, cosmetics, etc.

Note any odours at the sample sites, presence of natural surfactants, wind direction, temperature, conductivity, time and date, sequence of replicates.

Where appropriate fill and cap collection vials below the water surface with the mouth pointing upstream and position of sampler standing downstream.

For samples collected from a pipe allow the water to flush any non-steady state build up of volatiles for 2-5 min. and collect sample using minimum flow with the vial tilted to minimize aeration.

Upon filling the vial and securing the septum cap, invert the vial to check for headspace and possible leakage. If air bubbles are present top up the vial.

Store sample vials in a cooler with an ice pack at all times in the field. Ideal temperature is 4 C. Never freeze. (Check temperature of refrigerator during storage).

General Details on Sampling Procedures for Semi-volatile organic compounds

Collect batches of 1 L samples for all sample sites.

No preservative is added in the field. Methylene chloride is added in the laboratory on receipt of sample submissions (100 ml of MeCL per litre of sample).

Minimize exposure of the sample bottles to organic contamination from plasticizers, car exhaust fumes, solvents, cosmetics, plasticizers, etc.

Note any odours at the sample sites, presence of natural surfactants, organic phases, wind direction, temperature, conductivity, time and date, sequence of replicates.

For samples collected from a pipe allow the water to flush any non-steady state build up of organics for 2-5 min. before filling the sample bottle.

Store samples in a cooler with an ice pack at all times in the field. Ideal temperature is 4 C. Never freeze. (Check temperature of refrigerator during storage).

General Details on Sampling Procedures for Inorganic Compounds

Liquid Samples

Collect duplicate samples for all sample locations.

Collect a two liter aliquot.

Filter the entire two liters and mix to assure homogeneity.

Pour a portion of the filtered and mixed sample into a 500 mL HDPE bottle. Fill to the top with minimal headspace and secure tightly.

Pour a portion of the filtered and mixed sample into a 200 mL PSF bottle containing four mL of concentrated nitric acid. Fill to the top with minimal headspace and secure tightly.

Store all samples at 4°C.

Solid Samples

Collect dry solids samples in a wide-mouth glass or teflon bottle. Store samples under frozen conditions.

Collect wet samples in a wide-mouth glass or teflon bottle. Store at 4°C.

ATTACHMENT A-2

**PROTOCOL FOR THE SAMPLING OF
MONITORING WELLS**

DRAFT

CPA SOUR GAS PLANT REMEDIATION RESEARCH STUDY

PROTOCOL FOR THE SAMPLING OF MONITORING WELLS

2327-5-3

Sampling represents a potentially significant source of bias in groundwater-quality data. Erroneous data can result through a variety of causes. It is therefore imperative that proper sampling procedures be used to ensure that high quality, representative samples are collected. Recommended protocol for the various phases of the sample collection process are described below. Where applicable, these protocol shall also be applied to water samples taken from process treatment streams.

1. DEDICATED BAILERS

Dedicated PVC bailers have been installed at the site in all monitoring wells. These will minimize the risk for cross-contamination between wells. The following steps shall be followed when sampling for groundwater.

- (a) Ease the bailer into the standing water as free-falling bailers will cause de-gassing of the water upon impact.
- (b) While purging the wells, water shall be poured into 5 gallon pails to observe the potential presence of contaminants on the surface of the water. Note if contaminants are observed. Should the water be contaminated, make arrangements with the plant to dispose of the contaminated water properly.
- (c) Keep the bailer off the ground or other contaminated surfaces prior to insertion into the well.

2. PURGING THE WELL

Approximately the equivalent of 3 volumes of standing water shall be purged from the well prior to sampling. For a 50 mm (2") ID PVC well, installed in a 151 mm (6") hole with a sand pack, a 1 m height of standing water equals a volume of approximately 3 L. Above the screen, every metre of standing water represents 2 L of standing water, as there is no water bearing annulus above the screen depth. The dedicated bailers at Strachan hold 0.75 L of water.

When purging low yield wells, (wells incapable of yielding three standing volumes) wells should be bailed dry once and allowed to recover.

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3. FIELD PARAMETERS/SAMPLE COLLECTION

Measurements of electrical conductivity, temperature, and pH should be made at the monitoring point with portable equipment following purging and prior to sample collection. Measurement of Eh (Oxidation-reduction potential, redox potential) and dissolved oxygen shall also be carried out. These two tests require the use of a flow through cell, necessitating a pumping system (i.e. Grundfos submersible pump or Waterra) to achieve steady flow.

Samples shall be collected in order of the parameters' volatilization sensitivity (i.e. BTEX, DOC, metals, phenols, main ions).

The well shall be retested for pH, temperature, and conductivity following sampling as a means of checking the purging efficiency. If these measurements are significantly different, sample collection shall be postponed until additional purging and field measurements have been made.

4. SAMPLE PRESERVATION AND HANDLING

- (a) Routine Potability - 500 mL aliquot (plastic container)
- (b) DOC - 125 aliquot (plastic container)
- (c) Volatile Organics - Minimize air contact with sampled water by transferring directly from bottom of bailer to sample vials. A bottom fitted attachment should be used to obtain water sample from below a potential LNAPL layer at the top of the bailer. Fill (2) 40mL glass vials to the high meniscus. Turn upside down and tap. If bubbles are present, refill the vials.
- (d) Phenols - 125 mL glass aliquot, preserved with 2 mL of 12.5% H_2SO_4 .
- (e) Amines - 1 L glass aliquot
- (f) Metals - Samples shall be field-filtered through a 0.45 micron membrane filter, transferred to a 1L bottle, and preserved with 5 mL HNO_3 .

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5. STORAGE/SHIPPING OF SAMPLES

All samples should be stored in a cooler with ice, to maintain a temperature of 4°C. A maximum/minimum thermometer should be kept in the cooler to monitor temperatures during shipment to the laboratory. Maximum and minimum temperatures should be recorded on the chain of custody forms.

The maximum holding time prior to analysis for the following indicators is:

Volatile Organics, DOC, main ions, phenols	7 days
Oil and Grease (with HCl preservative)	28 days
Dissolved Metals (with HNO ₃ preservative)	6 months
Bacteria	24 hours

6. SAMPLING BLANKS/DUPLICATES

Trip Blanks - These pertain generally to volatile organic samples only. They are prepared prior to the sampling event in the actual sample containers and are kept with the other samples throughout the sampling event. There shall be one trip blank included in each sample shipping container.

Field Blanks - Should non-dedicated sampling equipment be used, field blanks should be obtained by running distilled water through the sample collection equipment after decontamination, and placed in the appropriate containers. This will determine the effectiveness of decontamination procedures.

Duplicates - For every group of samples, a minimum 5% duplicate samples shall be taken to monitor the precision of the lab results (i.e. two samples from the same bailer).

Duplicate samples shall be submitted under different monitor identification names, so that the analytical lab is unaware of their nature. If duplicate samples are submitted to different laboratories, then a minimum of three laboratories must be used.

Field Reference Standards (Blind Samples) - Accuracy of laboratory data may be confirmed by submitting samples with known parameter concentration prepared by an EPA-approved or equivalent source. These samples are submitted blind along with the

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natural samples. The exact amount of spiking material must be recorded to assess laboratory results. A high level of technical expertise from the field personnel is required to obtain useful information from this procedure. Five percent blind samples should be submitted.

Field Blanks - To monitor potential contamination from exposure to air, one sample per day should be collected with a sample container of distilled water opened and exposed at the site. The water sample shall be poured into appropriated containers to simulate actual sampling conditions. Analysis will be carried out for BTEX only.

7. CHAIN OF CUSTODY

A chain of custody form shall accompany all shipped samples to enable tracing of possession and handling of individual samples from the time of field collection through laboratory analysis. A copy must be kept for filing.

8. SAMPLE LABELLING

Samples must be labelled to prevent misidentification. The following information should be included on the labels.

- Sample identification number
- Project Job #
- Name of collector
- Date and time of collector
- Place of collection (i.e. piezometer number, process stream location, surface water body
- Parameters requested

9. FIELD LOGBOOK

Groundwater monitoring operations should be detailed in an up-to-date logbook that includes the following:

- Identification of well
- well depth
- static water level depth
- presence of immiscible layers

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- well yield (high or low)
- date and time well purged
- date and time of collection
- collection method for immiscible layers and sample I.D. numbers
- well sampling sequence
- types of sample containers used and sample I.D. numbers
- preservatives used
- parameters requested for analysis
- field observations on sampling event
- name of collector
- climatic conditions including air temperature
- internal temperature of shipping container

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