Chapter 7
Sampling & Analysis of Impacted Areas

7.1 Introduction

The purpose of this chapter is to introduce concepts and issues related to designing and implementing a sampling and analysis program for characterizing mining and mineral processing site waste management areas. This part of the planning process provides a path to prioritizing remedial actions and setting realistic goals, because it may not be possible to completely remove or remediate areas that may occupy many square miles

Section 7.2 will present general information about the sampling and analysis process. The individual tasks associated with sampling and analysis can be found in Chapters 3 and 4 of the *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA*[1]. The terms used in this chapter to identify sampling and analysis activities are those used in the guidance. For non-CERCLA actions the site manager is advised to consider CERCLA guidance in the context of site specific needs and circumstances.

Mining and mineral processing sites present many problems and issues that are not characteristic of other sites. Section 7.3 of the chapter will present unique characteristics of mining and mineral processing sites and briefly discuss how these characteristics can affect the sampling and analysis program. The remainder of the chapter will address issues associated with sampling and analysis at abandoned mining and mineral processing sites.

7.2 Sampling and Analysis

During the scoping process, any data for the site that is available will be collected, reviewed and analyzed, and the need for additional data defined. A sampling and analysis effort will likely be required to provide this additional data. A sampling and analysis plan (SAP) is a necessary part of the investigation and remediation process. This plan can be revised as sampling and analysis efforts are implemented.

The SAP is a document that specifies the process for obtaining environmental data of sufficient quality to satisfy the project objectives. Defining data quality objectives (DQOs) is the most important preliminary activity in creating an SAP. The DQO process offers site managers a way to plan field investigations so that the quality of data collected can be evaluated with respect to the data's intended use.

The outputs of the DQO process feed directly into the development of the two parts of the SAP: the quality assurance project plan (QAPP) and the field sampling plan (FSP). The FSP describes the number, type, and location of samples and the type(s) of field and analytical analyses; whereas the QAPP describes the policy, organizational, and functional activities necessary to collect data that will stand up to legal and scientific scrutiny. The SAP integrates the DQOs, FSP, and QAPP into a plan for collecting defensible data that are of known quality adequate for the data's intended use. More information on the tasks associated with generating the SAP can be found in Chapter 2 of the *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA*. Problems and issues that arise while creating and implementing the SAP will be discussed in the remainder of this chapter.

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[1] U.S. Environmental Protection Agency (EPA), October, 1988. *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA.* Washington, D.C. Office of Emergency and Remedial Response.

7.3 Issues for Sampling at Mining and Mineral Processing Sites

There are several important issues to consider in developing a sampling and analysis plan for an abandoned mining and mineral processing site. Mining sites may pose different sampling and analysis challenges than other hazardous waste sites contaminated by organic compounds and metals. The potential for widespread variable contamination is tremendous and the size of the site and volume of the contaminants can greatly complicate sampling and analysis efforts.

7.3.1 Defining Analytical Data Needs

This section briefly discusses analytical data needs and sources of analytical services for managing a sample analysis effort under the Superfund Program. Site managers of non-CERCLA investigations should select elements appropriate to their specific site. The key component in defining the analytical program needs for a mining and mineral processing site is to talk with fate and transport experts and environmental risk assessment experts to determine the forms of metals and other site contaminates (e.g., cyanide) that should be investigated. A clear understanding of the mining and mineral processing operations that have occurred on the site will greatly contribute to planning the investigation.

The particular type of data that needs to be generated depends on the project needs. The project needs are expressed as qualitative and quantitative DQOs which are developed in the project planning process.

Screening data. Screening data at mining and mineral processing sites can help to reduce initial sampling costs; analyses are conducted by rapid, less precise methods, with less rigorous sample preparation. Screening data provide analyte identification in the absence of historical site information. The x-ray fluorescence (XRF) analytical method is often used for screening data to increase the representativeness of the sampling quickly. See Section 7.3.7 of this chapter for more information on analytical methods and Appendix E for more information on the XRF method.

Definitive data. Definitive data are generated using rigorous analytical methods, such as approved EPA reference methods. Data are analyte-specific, with confirmation of analyte identity and concentration.

7.3.2 Understanding Pre-mining Conditions

At certain sites, the sampling plan can provide a useful tool to determine whether a release or threatened release represents conditions altered by human activity. This information could be used to determine whether a response action would trigger the exception contained in CERCLA section 104(a)(3)(A). That section restricts in certain respects the authority of the federal government to take a CERCLA response action in response to a release or threat of release "of a naturally occurring substance in its unaltered form, or altered solely through naturally occurring processes or phenomena, from a location where it is naturally found." This narrow exception applies where a release or threatened release is unaltered by human activity. Quite often, the impacts of mining are obvious, so a fairly simple sampling plan or site review can demonstrate that the releases are altered and therefore not covered by the exception contained in CERCLA section 104(a)(3)(A). If the exception does not apply, the degree of cleanup is governed by CERCLA section 121 and the NCP. Neither sections 104, 121, or the NCP require the agency to determine the pre-mining metal levels as a limit on the CERCLA response action. A review of natural background levels might in some case be considered in the analysis of ARARs or technical impracticability. In some instances, an investigation of the natural background condition can also assist the agency to determine the feasibility of achieving cleanup goals.

At mine sites, determining the pre-mining baseline condition can be a difficult or impossible task because mining activities often disturb mineralization in profound ways. Mining activities, such as removing overburden, tunnelling into the ground and removing ore, often expose previously protected mineralization to accelerated oxidation. These activities can also change ground water and surface water flow regimes, which can facilitate the release of metals into the environment.

Other factors also complicate efforts to determine pre-mining conditions at disturbed mineralized deposits. In many cases, mineralized areas are highly heterogeneous. Highly variable conditions reduces the ability to determine whether any particular area is undisturbed and representative of pre-mining, site-wide conditions. Moreover, ground water sampling efforts can disturb and expose the mineralization. This disturbance can elevate metal concentrations in the sample well above the levels present in an undisturbed condition, causing misleading results regarding the undisturbed condition. Moreover, efforts to associate releases to particular areas through metal ratios is complicated by seasonal variability and chemical and physical processes that occur as the water moves from the mineralized area to the sampling point. The unique nature of each mineral deposit also limits the ability to rely on undisturbed mineralized areas in other geographic locations as representative of the pre-mining conditions at the subject site.

Mineral processing activities can also complicate the study of pre-mining conditions. Mineral processing operations can deposit mine processing dust and waste over areas several square miles in size.

While statistical methods that rely on site chemistry may not be appropriate at most mine sites, in some cases non-chemical data can be used to infer pre-mining conditions. For example, evidence may indicate that prior to mining a stream supported aquatic life while after mining the stream does not support an aquatic community. This information would indicate that the pre-mining releases were relatively small relative to the post mining condition. Anecdotal evidence from the pre-mining period can also provide information regarding metal concentrations.

If chemical analysis will be used to differentiate unaltered naturally occurring releases from altered releases, it will be important to select appropriate “reference area” locations. A background sampling location should usually be upwind and upstream of the site. In other cases, a nearby watershed, unimpacted by mining, may provide an appropriate site for background water samples. In either case, the site should have soil characteristics and related properties similar to those that would have existed at an undisturbed portion of the site. If several different types of soil or habitats are present at the site, the site manager may need to gather more than one set of background data. The heterogeneous nature of mine sites, coupled with widespread contamination problems associated with mining, can greatly complicate reliance on a nearby reference site.

In selecting a reference area, the risk assessor should also consider anthropogenic contributors other than mining. For example, if a busy highway runs through a proposed background sampling area, the same or a similar highway should be associated with the mine waste site to account for leaded gasoline deposition. Locations that reflect obvious contributions of human activity, such as roadsides, drainage ditches, storm sewers, should generally be judged as inappropriate for collected background samples.

If background sampling is deemed necessary, it will be important to understand early in the process the ways in which the data will be used. For example, to ensure that spatially relevant and statistically significant results can be obtained, the assessor should design a plan to ensure that the assessor collects an adequate number of samples over an appropriate area and in a relevant pattern.

7.3.3 The Importance of Site Characterization

Prior to developing an actual sample collection strategy, proper characterization of the mining and mineral processing site should be conducted including:

Reconstructing pre-mining conditions;

Inventorying what has been deposited above-ground;

Obtaining records to determine the geology of areas where underground mining occurred;

Monitoring the movement of both surface and ground water; and

Estimating the impact of mining and mineral processing disturbances.

A thorough site characterization should include an understanding of the different mining and mineral processing processes that occurred since mining and mineral processing operations began. This type of information can be very helpful in anticipating all of the different types of waste that may be encountered at the site and determining where sampling should occur to obtain accurate data (see Chapter 2 for a discussion of mining and mineral processing processes). For example, milling operations generate very different wastes from smelting operations; and knowing which processes occurred at what time will help direct where samples should be taken and how they should be analyzed. A complete site characterization may also minimize sampling needs, thereby saving time and money.

There is a great deal of information available regarding historical mining and mineral processing sites that is helpful in site characterization. Mining companies may have significant background information from pre-mining exploration as well as information on how the site appeared before mining activities (This information may be important in developing long-term structurally stable cleanup plans). The information collected by the U.S. Geological Survey (USGS) and U.S. Bureau of Mines, now in the Office of Surface Mining (OSM), may be good sources of pre-mining site characterization data. State geologic or mining divisions also can have extensive historic mining databases. Historical production records from the mining and mineral processing operations may be kept by local historical societies. These records could provide tonnages, grades, and concentration methods. State mine inspector reports may also be used as a source of tonnage, grade and information on significant changes in the mining and mineral processing operations. Newspaper articles, books written about the mine or mining district, annual reports of mining and mineral processing companies, and work by government agencies may also provide information that will help determine where to sample, what contaminants to expect, and the range of concentration to anticipate.

Once the history of the mining and mineral processing site is characterized, the sampling strategies selected should be appropriate, based on pre-specified DQOs. Time consuming or expensive sampling strategies for some media may prohibit multiple sampling points; consequently it is important to balance the sampling objectives against the time and costs involved.

7.3.4 Calculating Preliminary Cleanup Goals

Preliminary Cleanup Goals (called Preliminary Remediation Goals (PRGs) under CERCLA) at mining and mineral processing sites can be used to focus cleanup efforts on a risk basis, concentrating sampling efforts in areas posing the highest risk hazards. Site specific cleanup goals can be calculated based on the environmental pathway at the site and the potential receptors. Setting preliminary cleanup goals is useful in focusing early action and site characterization goals while a site specific risk analysis is undertaken and should be included in large site cleanup projects.

Risk analysis efforts can be scaled back for smaller or more remote sites. PRGs may be useful in establishing detection limits required for analytical samples.

7.3.5 Selecting a Qualified Analytical Laboratory

Mining and mineral processing waste samples can pose unique analytical requirements. Samples often have a low pH level; contain several metals, often at high concentrations and varying solubilities; and vary widely in particle size. In selecting a qualified analytical laboratory, it is critical to consider the complexity of the sample matrix which will be analyzed. Site managers should select a laboratory that can handle the specific needs of their site and meet the established DQOs. Portable analytical laboratories , if used should be selected with the same criteria.

If an EPA Contract Laboratory Program (CLP) laboratory is selected, it is important to realize that the lab may not be experienced in analyzing mining and mineral processing waste. The routine sample preparation procedures and the pre-specified detection limits that the CLP process uses may not be applicable for mining and mineral processing waste samples. The site specific conditions will determine if a CLP laboratory is appropriate. These will include the need for specialized services, such as the acid-base account or humidity cells. In addition, if the concentration of contaminants in these samples is expected be orders of magnitude above the detection limit, the sample may not be accurately analyzed with the CLP procedures unless the lab is advised upfront. These factors are important when the site manager is considering what laboratory should perform the sample analyses for their specific site.

7.3.6 Determining the Leachability of Contaminants

The first critical step in selecting analytical methods appropriate to mining and mineral processing sites is the recognition that metal speciation is an important factor affecting the mobility and toxicity of metals at mining and mineral processing sites. Metals form different chemical compounds on the basis of their pH and oxidation-reduction potential, as well as the nature of the aqueous chemical environment. Different metal species form compounds with different solubilities, activities, toxicities, and environmental fates. Identifying these species at mining and mineral processing sites is extremely important in understanding a site, making assessments concerning environmental and human health risks, and arriving at reasonable decisions concerning cleanup actions. Interpretation of fate and transport potentials based on static and kinetic tests depends on the nature of the test (e.g., solvent duration) and the nature of the samples (e.g., tailings [fine particles, more surface area] versus some slag [coarse material, less surface area]).

The fate and transport of various chemical constituents from mining and mineral processing wastes can be evaluated by conducting static and kinetic tests. Tests can be used to determine if a waste is hazardous; the sample results depend upon the material(s) being tested. The most common test used internationally for mining and mineral processing waste samples is the Acid-Base Account. Since the 1970's variations of the Acid-Base Account have been used. These methods are based on measuring the total sulfur content in the sample to determine the amount of acidity that could be produced if all the sulfur were oxidized to sulfate and comparing the amount of acidity to the total buffering capacity of the rock. The test results can be used to determine the potential for metal leaching by computer analysis.

Other test methods are commonly used for conducting mining and mineral processing waste leachability analyses. These tests, however, may or may not be appropriate since they are conducted under saturated conditions (i.e., they do not measure the oxidation potential of sulfur bearing minerals). The primary RCRA test used to characterize waste samples is the Toxicity Characteristic Leaching Procedure (TCLP). Three potential alternatives to the TCLP exist: the Synthetic Precipitation Leaching Procedure (SPLP), which some states reportedly use; the Multiple Extraction Procedure (MEP); and California's Waste Extraction Test (WET). Some states use other methods; for example, Nevada uses the Meteoric Waste Mobility Test (MWMT) to assess the likelihood of acid generation over time. Additional information on the test methods discussed above can be found at the following:

- TCLP - http://www.epa.gov/epaoswer/hazwaste/test/1311.pdf;
- SPLC - http://www.epa.gov.80/epaoswer/hazwaste/test/1313.pdf;
- MEP - http://www.epa.gov.80/epaoswer/hazwaste/test/1320.pdf;
- WET - can be found in the California Code of Regulations, Title 22, Chapter 11, Article 5).

7.3.7 Selecting Analytical Methods

Many methods are available for the analysis of mining and mineral processing waste samples. The *Guide to Environmental Analytical Methods*[2] provides information on analytical methods, such as method detection limits, sample preservation requirements, field sample volumes required, and holding times. Examples of general analytical methods include total constituent analysis, acid digestion, X-ray fluorescence (XRF), and gas chromatography-mass spectroscopy (GCMS). Most of the methods mentioned in the Guide are included in SW- 846[3] EPA's test methods for evaluating solid waste. EPA's waste characterization data on Superfund mining and mineral processing sites[4] provides examples of sampling and analysis methods already used at selected mining and mineral processing sites. Exhibit 7-1 shows examples of analysis methods that have been chosen in the past.

Exhibit 7-1
Sampling and Analysis Methods

Method	Mining and Mineral Processing Site/Sample Matrix
Wet Chemistry/XRF	Cherokee County, KS. Galena Subsite: waste samples analyzed for metals
Acid Digestion	Cotter Uranium Mill, Canon City, CO: soil and sediment samples
XRF/ (Inductively Coupled Plasma Emission Spectroscopy (ICP))	Tex Tin Corporation, Texas City, TX: samples analyzed for lead, iron, nickel and tin initially using XRF did not show presence of metals; samples were then extracted with nitric acid and analyzed with ICP to confirm XRF results.

X-ray Fluorescence (XRF) Analytical Method

X-ray Fluorescence (XRF) is a non-destructive analytical technique used to determine the elemental composition of a sample. XRF measures the X-ray fluorescence coming from the inner electron shells of the atom. This is a systematic method and each element has its own "fingerprint". The XRF method measures the radiation coming direct from atoms and not from chemical compounds. The X-ray spectrum generated in the sample will tell which elements are present (wavelength of X-rays) and the amount of these elements (intensity of X-ray wavelength).

XRF is being applied to sites to increase the representativeness of sampling, expedite the activity by performing real-time data analysis to support decision making, and decrease both the time and

[2] Wagner, R.E., W. Kotas, and G.A. Yogis, 1992. *Guide to Environmental Analytical Methods*

[3] U.S. Environmental Protection Agency (EPA), 1986. *Test Methods for Evaluating Solid Waste (SW-846): Physical Chemical Methods.*

[4] U.S. Environmental Protection Agency, 1991. *Mining Sites on the National Priorities List: Waste Characterization Data.*

cost of these activities. Because of this, XRF is being considered at many abandoned mining sites. As with any method, application of the XRF method depends on the project objectives and associated DQOs. Representativeness and completeness are two of the major advantages of using XRF. On-site, real time chemical analysis can document representativeness and allows critical samples to be collected and analyzed, which typically ensures completeness.

Media that are commonly appropriate for XRF analysis include soils, in particular, but essentially all solids, as well as liquefied solids, such as sludges and slurries. Detection limits extend from mg/kg (parts per million) to the 100 percent range for mobile XRF instruments and from tens to hundreds of mg/kg to 100 percent for field portable instruments.

Field-portable instruments, usually weighing less than 20 pounds (including batteries), can be carried to the sample location. Mobile instruments, however, require line voltage, and are usually placed within a specific building or van near or at the site to generate quality data. Decisions concerning the attainment of an action level can be made quickly at the site. Coupling the use of a field portable and mobile laboratory instruments at a site would allow for almost immediate decisions to be made concerning an action level in the field that can be confirmed by the mobile laboratory. Typically, a representative composite sample from the site area under cleanup action is sent to the laboratory for final documentation of the clean up level.

In most instances, an initial set of site samples is required for calibration purposes. The samples should cover the matrices and concentration range of elements of concern as determined by a total metals analysis by a laboratory. The samples should be prepared by the laboratory using the same protocol that will be used with the XRF at the site.

At the sample location, a field-portable instrument is equipped with a probe that allows considerable flexibility in how a sample is presented to the source. The source may be pressed against the media of interest (soils, tailings, walls, etc.) or a sample cup of material (soil, slurry, sludge, etc.) can be placed on top of the source. Samples may be sieved or pulverized but sample preparation is typically minimal. Field-portable instruments are versatile but have the highest detection limits of the three types of instruments. Typical detection limits with little to no sample preparation are in the 100 mg/kg range, depending on sample matrix. For mobile instruments, sample preparation is part of the analytical schedule and includes sieving and pulverizing. A typical detection limit will range from 5 to 30 mg/kg, depending on the sample matrix. Sample preparation and particle size variance are major potential sources of error.

High expectations and indiscriminate use of the instruments outside the design limits of the unit has sometimes led to discouragement in the application of field-portable XRF instruments. Although a particularly low detection limit may not be achievable in some cases, the instrumentation will usually determine hot spot areas, document that representative sampling has been accomplished, and determine that an action-level for a particular element has been reached in real time at the location. Confirmatory analyses should be performed by a fixed analytical laboratory.

The total extent of XRF application to abandoned mining sites is undoubtedly larger than the published accounts of such applications. Documented use of field-portable XRF instruments start in 1985 with the Smuggler Mountain Site near Aspen, Colorado.[5] The instrument was used to determine action-level boundaries of 1,000 mg/kg lead and 10 mg/kg cadmium in soils and mine waste. The same site was used for the evaluation of a prototype field-portable XRF instrument

[5] Mernitz, S., Olsen, R., and Staible, T., 1985, Use of Portable X-Ray Analyzer and Geostatistical Methods to Detect and Evaluate Hazardous Materials in Mine/Mill Tailings: Proc. Natl. Conf. on Management of Uncontrolled Hazardous Waste Sites, Washington, DC, pp. 107-111.

specifically for hazardous waste screening[6]. Field-portable instruments have also been used at the California Gulch Site, Leadville, Colorado; Silver Bow Creek and other sites near Butte, Montana; Bunker Hill Site, near Kellogg, Idaho; and the Cherokee County Site, Tri-State Mining District, Kansas for screening purposes during site characterization. A field-portable instrument has been used to screen a large area (21 square miles) to select large, homogeneous volumes of heavily contaminated soils for treatability studies and for Site Comparison Samples at the Bunker Hill Site.[7] Portability and "real-time" basis data were necessary prerequisites. A mobile XRF instrument was used for multi-element analysis of lead, arsenic, chromium, and copper in soils.[8] Detection limits with the x-ray-tube-source and Si(Li) detector were as low as 10 mg/kg. The data were used to map the extent of contamination within a superfund site. Detection limits for field-portable instruments are not low enough to determine cadmium concentrations as low as 10 mg/kg in some areas/matrices, but zinc was found to be a good surrogate indicator element for cadmium in Cherokee County, Kansas.

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[6] Raab, G.A., Cardenas, D., Simon, S.J., and Eccles, L.A., 1987, Evaluation of a Prototype Field-Portable X-Ray Fluorescence System for Hazardous Waste Screening: EMSL, EPA 600/4-87/021, U.S. Environmental Protection Agency, Washington, DC, 33 p.

[7] Barich, III, J.J., Jones, R.R., Raab, G.A., and Pasmore, J.R., 1988, The Application of X-Ray Fluorescence Technology in the Creation of Site Comparison Samples and in the Design of Hazardous Waste Treatment Studies: First Intl. Symposium, Field Screening Methods for Hazardous Waste Site Investigations, EMSL, Las Vegas, NV, pp. 75-80.

[8] Perlis, R., and Chapin, M., 1988, Low Level XRF Screening Analysis of Hazardous Waste Sites: First Intl. Symposium, Field Screening Methods for Hazardous Waste Site Investigations, EMSL, Las Vegas, NV, p. 81-94.