Tech Note[1]
Mining Waste Characterization

Characterization of Solid Mining Waste

The California Water Code (CWC) requires that any person discharging waste, or proposing to discharge waste, that could affect the quality of the waters of the state, to file a report of waste discharge ((ROWD) (CWC 13260)). The Water Code has additional requirements for mining waste, including a report on the physical and chemical characteristics of the waste that could affect its potential to cause pollution or contamination. A technical report is also required that evaluates the potential of the discharge of the mining waste to produce, over the long term, acid mine drainage, the discharge or leaching of heavy metals, or the release of other hazardous substances (CWC 13260(k)). This technical report should also evaluate the potential of salt loading from mining waste material (sulfate, nitrate, ammonia, etc.).

Collection of field samples and subsequent testing of the expected mining waste should be based on clearly defined objectives identified in a **sampling plan** prepared by professional(s) registered to practice in California in the field of engineering or geologic sciences. While there is no specific set of rules for the report on the physical and chemical characteristics of the mining waste, initial characterization is typically carried out by laboratory determination of metal concentrations, acid generation potential, and metals leachability. A frequent starting point for characterization has been laboratory analysis of Total Threshold Limit Concentrations (TTLCs) of CAM-17 Metals (California Code of Regulations Title 22, Section 66261.24) in accordance with EPA Test Methods for Evaluating Solid Waste, Revised Methods SW-846 as shown in Table 1.

Table 1. CAM-17 Metals (TTLCs)

Analyte	**Analytical Method**	Target Method Detection Limit (mg/kg)
Antimony	EPA 6010	2
Arsenic	EPA 6010	2.5
Barium	EPA 6010	0.2
Beryllium	EPA 6010	0.2
Cadmium	EPA 6010	0.2
Chromium	EPA 6010	0.6
Cobalt	EPA 6010	0.6
Copper	EPA 6010	1
Lead	EPA 6010	0.75
Mercury	EPA 7470	0.02
Molybdenum	EPA 6010	0.8
Nickel	EPA 6010	1
Selenium	EPA 6020	4
Silver	EPA 6010	0.5
Thallium	EPA 6010	1.5
Vanadium	EPA 6010	0.5
Zinc	EPA 6010	1

[1] This document is an informational document describing some Regional Water Board needs for mine waste characterization. Other sampling protocols and procedures can be submitted in a Mining Waste Characterization Plan and implemented with Regional Water Board staff concurrence.

Soluble Threshold Limit Concentrations (STLCs)

Since it is the soluble fraction of a constituent of a solid waste, which actually has the potential to migrate to waters of the State, the **extractable** concentration is a more accurate measure (than the total concentration) of the ability of a particular solid waste constituent to degrade water quality. The California modified Waste Extraction Test (WET) procedure is used to provide a measure of the leachability of solid samples to release metals into solution. Extractable concentrations from the WET are expressed in milligrams per liter (mg/l) of extract, rather than milligrams per kilogram (mg/kg) of waste as shown below in Table 2. The analyte list, associated analytical methods, targeted method detection limits (MDL), minimum sampling volumes, sample preservation, and holding time requirements for STLC analysis are listed in Table 2.

Table 2. CAM-17 Metals (STLC)

Analyte	Analytical Method	Target Method Detection Limit (mg/kg)[2]	Target Method Detection Limit (mg/l)[3]	Holding Time (days)	Minimum Sample Volume	Preservation
Antimony	WET[1]/EPA 6020 EPA 3050b/EPA 6010	2	0.0002	180		
Arsenic	WET[1]/EPA 6020 EPA 3050b/EPA 6010	2.5	0.0005	180		
Barium	WET[1]/EPA 6020 EPA 3050b/EPA 6010	0.2	0.0001	180		
Beryllium	WET[1]/EPA 6020 EPA 3050b/EPA 6010	0.2	0.0001	180		
Cadmium	WET[1]/EPA 6020 EPA 3050b/EPA 6010	0.2	0.0001	180		
Chromium	WET[1]/EPA 6020 EPA 3050b/EPA 6010	0.6	0.00005	180		
Cobalt	WET[1]/EPA 6020 EPA 3050b/EPA 6010	0.6	0.00005	180		
Copper	WET[1]/EPA 6020 EPA 3050b/EPA 6010	1	0.0005	180	225 g for each WET and EPA 3050b	Small samples: Cool at 4º C for transport, no preservation needed
Lead	WET[1]/EPA 6020 EPA 3050b/EPA 6010	0.75	0.0001	180		
Mercury	WET[1]/EPA 3050b/EPA 7470	0.02	0.0002	28		
Molybdenum	WET[1]/EPA 6020 EPA 3050b/EPA 6010	0.8	0.0001	180		
Nickel	WET[1]/EPA 6020 EPA 3050b/EPA 6010	1	0.0002	180		
Selenium	WET[1]/EPA 6020 EPA 3050b/EPA 6010	4	0.0015	180		
Silver	WET[1]/EPA 6020 EPA 3050b/EPA 6010	0.5	0.00005	180		
Thallium	WET[1]/EPA 6020 EPA 3050b/EPA 6010	1.5	0.00005	180		
Vanadium	WET[1]/EPA 6020 EPA 3050b/EPA 6010	0.5	0.00005	180		
Zinc	WET[1]/EPA 6020 EPA 3050b/EPA 6010	1	0.002	180		

[1] Wet test modified to use DI water instead of citric acid when appropriate (results of the acid-base account indicate which extraction solution should be used in the WET).
[2] Target Method Detection Limits (mg/kg) for Total Metals (EPA SW-846 3050b/6010).
[3] Target Method Detection Limits (mg/l) for WET leachate analysis (EPA 6020).

Acid Mine Drainage

Acid mine drainage results from the weathering of sulfide minerals. These sulfur containing minerals become oxidized when waste materials are exposed to air for the first time. The oxidation process produces sulfurous acid (H_2SO_3), a major component of acidic leachate, which can readily mobilize metals in mining waste. However, minerals such as calcium carbonate ($CaCO_3$) may also be present in the mining waste, which have sufficient capacity to neutralize the acid formed from oxidation of sulfide minerals. In order for the waste to be able to produce acid, the ability of the waste to generate acid must exceed its ability to neutralize acid over the life of the waste.

The potential of a waste to produce acid leachate is termed the "acid generation potential" (AGP), while the ability of a waste to neutralize acid is called the "acid neutralization potential" (ANP). AGP may be expressed in pounds of $CaCO_3$ required to neutralize the acid formed by 1,000 pounds of waste; while ANP may be expressed in pounds of $CaCO_3$ equivalents per 1,000 pounds of waste. When expressed in these terms, the ratio of ANP to AGP is a measure of the overall ability of the waste to produce acid. This type of testing is commonly referred to as **static testing** and is used as a screening tool and any implications are subject to further verification.

A ratio of ANP to AGP of less than 3:1 indicates that an acidic leachate may be formed, while a ratio of ANP to AGP of 3:1 or greater indicates that an acidic leachate will probably not be formed by the waste. However, further analysis may or likely be required using **kinetic testing,** which would help determine the mining waste potential for long term acid generation. Analytical procedures exist for determining AGP and ANP, and thereby determining the overall acid-base account, of a waste as shown in Table 3.

Table 3. Analysis Parameters and Methods for Acid Base Accounting of Solid Samples.

Analysis	Analytical Method	Minimum Sample Volume (g)	Preservation
pH (paste)	USDA No. 60 (21a)		
Acid Neutralization Potential (ANP)	EPA 600 ($CaCO_3$ Equiv./Titration)		
Acid Generation Potential (AGP)	LECO Combustion IR[1]		Soil: Cool at
Non-extractible Sulfur, S	LECO Combustion IR[1]	225	4º C for
Pyritic Sulfur, S	LECO Combustion IR[1]		transport, no
Sulfate Sulfur, S (HCL Extractible)	LECO Combustion IR[1]		preservation
Total Sulfur, S	LECO Combustion IR[1]		needed.

[1] Modified Sobek method used to determine the acid-base account of the waste.

The results of the acid-base account indicate which extraction solution should be used in the Waste Extraction Test (WET). The WET uses a citrate buffer solution with a pH of 5.0 to mimic the extraction capability of 'nonhazardous solid waste' leachate, which is often acidic. The citrate buffer is appropriate for any waste, which has an ANP to AGP ratio of less than 3:1. Deionized water could be substituted for the citrate buffer for wastes having an ANP to AGP ratio of 3:1 or greater. In some cases, it may be appropriate to adjust the deionized water to the pH of local rainwater to be able to assess the resulting leachability of waste constituents.

Surface Water and Groundwater Characterization

Surface water and groundwater characterization should include all waste constituents, reaction products, and hazardous constituents that are reasonably expected to be in or derived from the

mining wastes. The CAM-17 metals list can be used as a starting point and should be modified as appropriate to include known or suspected mineralization at the site. A suggested constituent list and analytical methods is shown in Table 4. These laboratory test methods and detection limits are based on the Central Valley Regional Water Quality Control Board criterion quantitation limits pursuant to the Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California, 2005 (SIP).

Table 4. Laboratory Constituent List for Surface Water and Groundwater Samples

Constituent	EPA Method	Target Method Detection Limit (mg/l)
Aluminum, total and dissolved	M200.7 ICP	0.03
Antimony, total[1] and dissolved[2]	M200.8 ICP-MS	0.0004
Arsenic, total and dissolved	M200.8 ICP-MS	0.0001
Barium, total and dissolved	M200.8 ICP-MS	0.0001
Cadmium, total and dissolved	M200.8 ICP-MS	0.0001
Chromium, total and dissolved	M200.8 ICP-MS	0.0001
Cobalt, total and dissolved	M200.8 ICP-MS	0.00005
Copper, total and dissolved	M200.8 ICP-MS	0.0005
Iron, total and dissolved	M200.7 ICP	0.02
Lead, total and dissolved	M200.8 ICP-MS	0.0001
Manganese, total and dissolved	M200.8 ICP	0.005
Mercury, total and dissolved	M245.1	0.0002
Nickel, total and dissolved	M200.8 ICP-MS	0.0006
Silver, total and dissolved	M200.8 ICP-MS	0.0001
Thallium, total and dissolved	M200.8 ICP-MS	0.0001
Vanadium, total and dissolved	M200.8 ICP-MS	0.0002
Zinc, total and dissolved	M200.8 ICP-MS	0.002
Calcium, dissolved	M200.7 ICP	0.2
Magnesium, dissolved	M200.7 ICP	0.2
Sodium, dissolved	M200.7 ICP	0.3
Potassium, dissolved	M200.7 ICP	0.3
Chloride, dissolved	M325.2	1
Bicarbonate, dissolved	M2320B-Titrametric	2
Carbonate, dissolved	M2320B-Titrametric	2
Total Alkalinity, dissolved	M2320B-Titrametric	2
Silica, dissolved	M200.7 ICP	0.2
Sulfate, dissolved	M300.0	10
Nitrate/Nitrite as N, dissolved	M353.2	0.02
Ammonia (as N)	M350.1	1.5
WAD Cyanide	SM4500-CN	0.01
pH	M150.1 - Electrometric	0.1 su
Conductance	M120.1 - Meter	1 umhos/cm
Total Dissolved Solids	M160.2	10
Total Suspended Solids	M160.2	10
Hardness (as $CaCO_3$)	M130.2	5

[1] If overland flow to surface waters is possible, the **total** constituent concentrations may be available for movement and analyses should be conducted on unfiltered samples.

[2] Only the **dissolved** concentrations of waste constituents are available to migrate through soils to ground or surface waters.

Reports

Any technical report required that involves planning, investigation, evaluation, engineering design, or other work requiring interpretation and proper application of engineering or geologic sciences shall be prepared by or under the direction of persons registered to practice in California pursuant to California Business and Professions Code sections 6735, 7835, and 7835.1. As required by these laws, completed technical reports must bear the signature(s) and seal(s) of the registered professional(s) in a manner such that all work can be clearly attributed to the professional responsible for the work.