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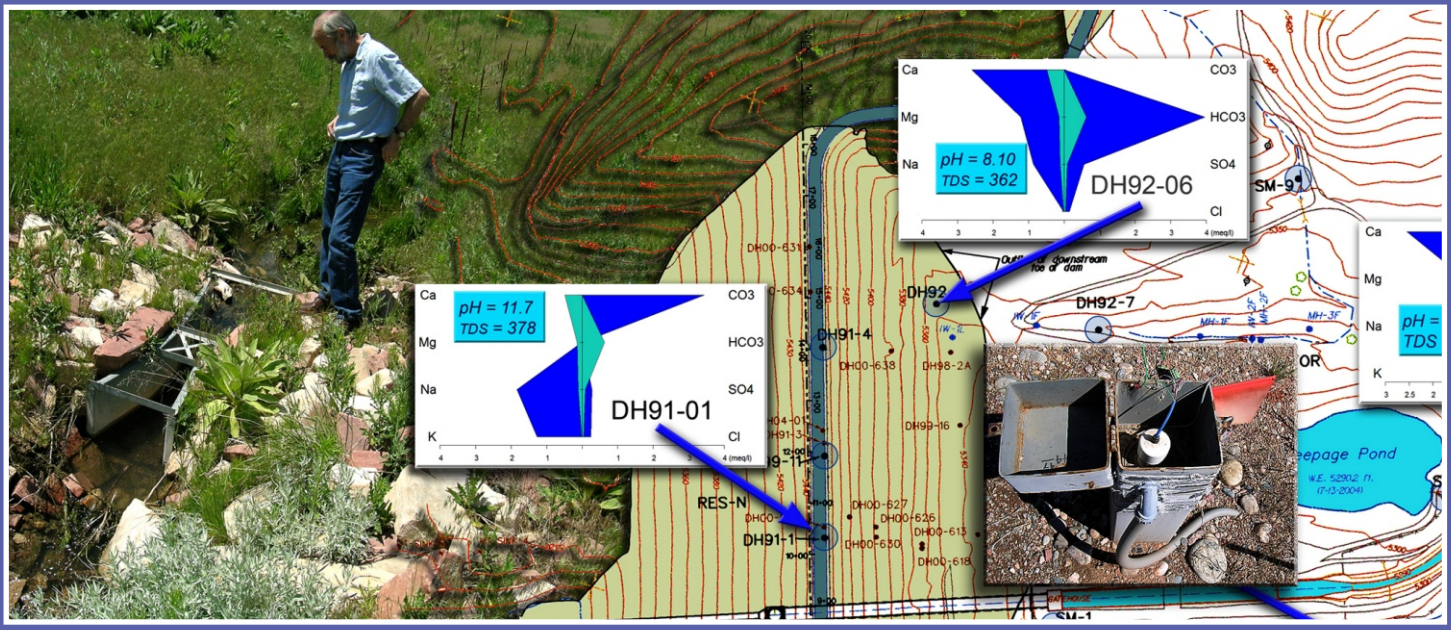
Managing Water in the West

Report DSO-05-03

Seepage Chemistry Manual



Dam Safety Technology Development Program

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14. ABSTRACT
Gypsum, anhydrite, calcite, dolomite, and halite are soluble minerals that are common in the western United States where the Bureau of Reclamation has constructed many dams. Dams sited on foundations and abutments containing soluble minerals have the potential to develop seepage problems that require monitoring by water resource managers. When mineral dissolution is suspected at a dam, seepage samples may be collected, analyzed and compared to reservoir water to help determine whether soluble minerals pose a structural safety problem. Seepage chemistry investigations are interdisciplinary and require collaboration among chemists, geologists, engineers, and geophysicists. This peer reviewed technical report summarizes the basic chemistry associated with mineral dissolution, weathering, biotic processes and mixing, all of which may contribute to changes in seepage chemistry during structural transit. This report also provides references and good practice procedures to guide seepage chemistry investigations, and includes examples from successful seepage investigations performed over the past 20 years by Bureau of Reclamation Dam Safety Program professionals.

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Seepage Chemistry Manual

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Mission Statements

The mission of the Department of the Interior is to protect and provide access to our Nation's natural and cultural heritage and honor our trust responsibilities to Indian Tribes and our commitments to island communities.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

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Executive Summary

Gypsum, anhydrite, calcite, dolomite, and halite are soluble minerals that are common in the western United States where the Bureau of Reclamation has constructed many dams. Dams sited on foundations and abutments containing soluble minerals have the potential to develop seepage problems that require monitoring by water resource managers and engineers responsible for dam safety issues. When mineral dissolution is suspected at a dam, seepage water samples may be collected and analyzed and compared to reservoir water to help determine whether soluble minerals pose a structural safety problem.

Seepage chemistry investigations are interdisciplinary and require collaboration among chemists, geologists, engineers, and geophysicists. This report summarizes the basic chemistry associated with mineral dissolution, weathering, biotic processes and mixing, all of which may contribute to changes in seepage chemistry during structural transit. This report also provides references, overviews of planning, sampling, quality assurance, and interpretation of seepage chemistry investigations, and examples from successful seepage investigations performed over the past 20 years by Bureau of Reclamation Dam Safety Program professionals. Summary references are also recommended for the reader who wishes to investigate specific topics more thoroughly.

Besides a general overview of seepage geochemistry, helpful reference information is also provided in the appendices. Appendix 1 summarizes field sampling resources, sample submittal and chain of custody forms, sources for field and sampling equipment, and sources for analytical and technical services for seepage geochemistry investigations. Mineral saturation index calculations using the MINTEQA2 chemical equilibrium model are discussed and a standard operating procedure for running the MINTEQA2 model is provided in appendix 2. Development and application of mass balance models, a standard approach used by geochemists, is presented and example mass wasting and void formation calculations are included in appendix 3. Appendix 4 shows a pictorial guide for collecting seepage samples from piezometer wand observation wells. A technical glossary and unit conversion factors are also presented in appendix 5.

Introduction

Dam Safety and the Bureau of Reclamation

Established in 1902, the Bureau of Reclamation (Reclamation) is a federal water resource management and development agency that operates in the 17 Western States under the Department of the Interior (DOI). Reclamation constructed and is responsible for management of 348 storage reservoirs impounded by 471 dams and dikes (Reclamation, 2005a) that provide water for agricultural, residential, municipal, and industrial uses to more than 31 million people in the arid West. Reclamation provides irrigation water to one out of five Western farmers (or 140,000 farmers), tilling 10 million acres of farmland that produce 60 percent of the nation's vegetables and 25 percent of its fruits and nuts. Reclamation also operates 58 hydroelectric powerplants with annual average power generation of 42 billion kilowatt-hours (DOI, 2005).

Because of the potential threat to the public posed by dam failures, Reclamation's Dam Safety Program was officially implemented in 1978 with passage of the Reclamation Safety of Dams Act, Public Law 95-578. This act was amended in 1984 under Public Law 98-404. Program development and administration of safety of dams activities is the responsibility of Reclamation's Dam Safety Office located in Denver, Colorado (Reclamation 2005b). Reclamation's dam safety activities are also coordinated under the National Dam Safety Program managed by the Federal Emergency Management Agency (FEMA) (FEMA, 2005).

What Is Seepage?

In this manual, seepage can be defined as water emerging from surface wet spots or flowing springs near or downstream of dams. The geologic materials in the foundations (beneath the dam) and abutments (on the ends of dams) are usually not watertight or uniform, so impounded reservoir water flows underground, around and under the dam, through permeable or semiporous rock, along fractures and cracks, voids, faults, and joints between local geological strata. Seepage is a reservoir-influenced groundwater in the immediate vicinity of the dam that follows the flow paths of least resistance (or highest permeability) in the foundation or abutment rock, and that flows in response to the hydraulic pressure (head) exerted by the depth of the reservoir water behind the dam.

Seepage flow around and below a dam is a complex and dynamic groundwater environment because of two primary factors: geological complexity (heterogeneity), and seasonally changing reservoir elevations.

In porous geological formations, multiple seepage flow paths and variable permeability zones may exist. Confined seepage paths with a small flow cross section (a small diameter "pipe") can be short and direct with corresponding short seepage underground residence time (transit time), or long and serpentine with longer transit times. Diffuse seepage paths through permeable geology (with large flow cross sections) usually experience longer transit times and behave more like typical groundwater.

Reservoirs in the West usually experience highest reservoir surface elevation and maximum head after snowmelt runoff in the spring, and lower heads during fall and winter. Both confined and diffuse seepage paths exhibit *time-lagged* flow response to changes in reservoir head. Seepage flow may not increase immediately when reservoir elevation rises, and some seeps flow well after reservoir elevation has dropped. In general, a seep that responds quickly to resevoir elevation changes suggests a direct hydraulic path from the reservoir to the seep that should be monitored carefully.

> *"All dams leak."*
> William Mulholland, March 11, 1928, while inspecting seepage at St. Francis Dam (Leslie, 1993)

Because all hydraulic structures and foundations experience seepage, engineers anticipate the power of seepage water pressures and design drainage systems to control seepage. Drains reduce seepage pressures in the foundation and safely direct seepage to outfalls. In fact, earthen dams are designed to safely allow seepage to pass through the compacted earth structure itself, to be collected in drains located along the toe of the dam. As long as the seepage is not severe (flowing with heavy suspended particle loads), is stable (not increasing or progressing), and removed through effective drainage, it usually poses no problem to the structural stability of the dam.

However, as the ironic quotation by William Mulholland suggests—made 24 hours before the failure of St. Francis Dam near Saugus, California—ignoring progressive (increasing) seepage at a dam can have disasterous consequences. One of the primary ways that a dam or dike can fail is when seepage flows in the foundation or abutments near the dam increase over time and lead to erosive seepage called piping. Once piping begins, seepage flow paths enlarge, the erosive force of the seepage increases under the reservoir head, and materials supporting the dam—or embankment materials themselves—are washed away. These rapidly increasing voids usually lead to the catastrophic failure of the dam.

What Is Mineral Dissolution?

Gypsum, anhydrite, calcite, dolomite, and a variety of other simple minerals are water soluble and common to the geology of the western United States. Because these minerals are common, they are often found in the foundations and abutments of many Reclamation dams. It may seem odd that materials we think

of as “rock” can actually dissolve in water, but it really does happen. Most caves and caverns in limestone were created when groundwater dissolved the mineral calcite ($CaCO_3$) and left behind void spaces (Ford and Ewers, 1978).

When soluble minerals present in the foundation or abutments of dams are dissolved by seepage water, the void spaces that form can lead to greater permeability and flows along established flow paths, or the development of new seepage flow paths. If the seepage progresses, excessive flows may develop that lead to erosion and piping and eventual structural failure. Increasing seepage volumes near embankments have often been associated with structural failure and downstream flooding (Cedergren, 1989; James and Lupton, 1978; James and Kirkpatrick, 1980; James, 1985; Maksimovich and Sergeev, 1983; Muckenthaler, 1988), so determining the extent and nature of mineral dissolution should be a priority in dam safety assessments where seepage is a concern.

What Is Seepage Chemistry?

Seepage chemistry is a term used in this report that refers to the set of measured concentrations of chemical constituents in seepage water. These measured constituents in seepage water (or seepage concentrations) can be compared to the chemistry of the reservoir water (the reservoir concentrations) to evaluate whether changes between the reservoir and seepage chemistry are caused by mineral dissolution. However, the evaluation of changes in seepage relative to reservoir is not simple because increases may be the result of several concurrent processes: mineral dissolution; mixing of seepage with a higher concentration, local, preimpoundment groundwater; delayed emergence of higher concentration reservoir water; or bacterial processes. A careful assessment of reliable seepage chemistry data is needed to distinguish causes for increased seepage concentrations.

Seepage chemistry investigations are therefore inherently interdisciplinary and require the coordination of information from several fields: analytical chemistry, geochemistry, hydrology, geophysics, and civil and geotechnical engineering. While monitoring structures with dam safety concerns, seepage flow dynamics and piezometer elevation data should be the principal focus. However, chemical analysis of reservoir and seepage water can provide important information concerning the influence of mineral dissolution on seepage. Seepage chemistry has been used to help evaluate mineral dissolution since 1951, when downstream seeps began flowing after first filling of the reservoir at at Horsetooth Dam, Fort Collins, Colorado.

This manual provides engineers and nonchemists working on dam safety assessments an overview of mineral dissolution and other processes that can change the chemistry of seepage water. Also included are guidance for planning seepage chemistry investigations, procedures for collection and analysis of samples, resources for analytical chemistry testing and other diagnostic testing

services, guidelines for seepage chemistry quality assurance and data quality evaluation, and an overview of geochemical interpretation techniques routinely applied to seepage chemistry data.

Chemistry Concepts

This section provides a review of concepts relating to solubility, chemical equilibrium, water chemistry, and the ways that mineral dissolution fits into the theoretical chemistry framework.

What Is Solubility?

We all have an intuitive understanding of what solubility means. It is when a solid, liquid, or gas (called the *solute*), dissolves in a liquid (called the *solvent*), to form a homogeneous mixture called a *solution*. With seepage, we are concerned with aqueous solutions, which are defined as mixtures of solutes in water. In dam seepage, the solutes are minerals present in the foundation, abutments, and embankment, and atmospherically and biologically produced gases. The solvent is usually reservoir water, though percolating rainwater and any other local groundwater may also act as the solvent. Simple dissolution can occur in one of two ways:

- *Electrolytes (compounds with ionic bonds).*—The solute can be an ionic compound or salt that *dissociates* to form two oppositely charged *ions* when placed in water. A salt dissociates into a positive ion (*cation*) and a negative ion (*anion*) when placed in water, and these ions can conduct electricity. Thus, measurement of the electrical conductivity in water is related to the concentration of dissolved electrolytes.

- *Nonelectrolytes (compounds with covalent bonds).*—The rule of solubility is "like dissolves in like," so nonelectrolytes that have an electrical dipole (*polar* compounds) tend to dissolve in water (which has an electrical dipole and is also polar). In this case, the solute forms a *hydration layer* of water molecules around the compound molecule that makes it stable in aqueous solution. Nonelectrolyte solutes include amorphous silica glass (SiO_2) and polar organic (carbon-containing) compounds such as sugars, ethanol, and other organic compounds with functional groups (organic acids, bases, alcohols, aldehydes, or ketones). Gases are another group of nonelectrolytes important to dam seepage chemistry. Natural waters and seepage contain dissolved atmospheric and biologically produced gases such as oxygen (O_2, called dissolved oxygen or DO in water), nitrogen (N_2), and carbon dioxide (CO_2). CO_2 affects the carbonate-bicarbonate-pH equilibrium (*alkalinity*) in water, and thus may also affect the solubility of carbonate rocks like calcite

and dolomite. Other gases that are byproducts of bacterial activity may also be dissolved in seepage, such as hydrogen sulfide (H_2S) and methane (CH_4).

Primary Variables Affecting Aqueous Solubility

Several variables and properties associated with water affect the solubility of minerals and other solutes. These include pH, the oxidation-reduction conditions, temperature, pressure, and the other solutes (chemical constituents) in the solvent water.

pH—Hydrogen Ion Activity

One of the most important variables is pH, which represents the amount of free hydrogen ion (H^+, or protons) in water solutions. pH is defined as the inverse of the base-10 logarithm of the hydrogen ion *activity* (concentration in moles per liter (mol/L), adjusted for solution equilibrium factors), and is based on the dissociation of pure water into the hydrogen ion (H^+) and hydroxide ion (OH^-):

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \text{Eq. 1}$$

When this reaction reaches equilibrium at standard temperature and pressure (273 °K, 1 atm), the activities of both H^+ and OH^- are 1×10^{-7} mol/L. From this, a pH of 7 is considered neutral. The pH scale varies from 0 to 14, with values below 7 representing *acidic* conditions, and values above 7 representing basic or *alkaline* conditions. Acidic waters dissolve solutes that are bases, and alkaline waters dissolve acidic solutes. The pH of pure water in equilibrium with the atmosphere is less than 7, caused by dissolved CO_2 forming bicarbonate ion (HCO_3^-), carbonic acid (H_2CO_3), and H^+. Rain is therefore slightly acidic and tends to dissolve carbonate minerals, which are bases.

pE and Eh—Free Electron Activity

Another important water quality variable affecting the solubility of minerals is the *oxidation-reduction potential* (ORP), or *redox* potential. Called *pE*, this represents the activity (equilibrium-adjusted concentration) of free electrons in water, denoted as [e^-] and is analogous to pH. Free electrons and protons do not actually exist in water, but the concept is useful as a summary: *reducing* water has an abundance of [e^-], while an *oxidizing* water has very low [e^-]. In natural waters, redox is actually controlled by two primary influences: mixing with O_2 from the atmosphere (DO), and bacterial activity. Water can be *oxidizing* or *reducing* (analogous to acidic and basic), and each redox state encourages specific reactions.

Water containing DO is oxidizing, and these conditions favor:

- Breakdown of organic compounds

- Precipitation of iron (Fe) and manganese (Mn) as insoluble compounds called oxyhydrates

- Chemical species with higher oxidation states—Fe^{3+} (+III oxidation state); Mn^{3+} (+III); CO_2 (+IV); nitrate, NO_3^- (+V); and sulfate, SO_4^{2-} (+VI)

- Dissolution of reduced solutes such as pyrite, ferrous sulfide (FeS_2^{2-})—the acid mine drainage reaction (Manahan, 1994):

$$\overset{pyrite}{2FeS_2^{2-}} + 2H_2O + 7O_2 \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \qquad \text{Eq. 2}$$

Once DO is depleted, water becomes reducing and favors:

- Preservation of organic compounds

- Reduction of Fe- and Mn-oxyhydrates and release of Fe, Mn and other trace elements adsorbed to oxyhydrates

- Chemical species with lower oxidation states—Fe^{2+} (+II); Mn^{2+} (+II); CH_4 (-IV); ammonia, NH_3 (-IIIV); and sulfide, S^{2-} (-II)

Redox is usually measured with a platinum electrode in millivolts (mV), called Eh, with values above 0 mV representing oxidizing conditions and negative values representing reducing conditions. Readings with a platinum electrode, however, are not reliable in waters with DO because of several other redox reactions occurring at the platinum-H_2O interface. Natural waters support many chemical reactions sensitive to pH and pE, and the overall Eh of water depends on the interaction of many redox reactions. Computer chemical equilibrium models, such as PHREEQE or MINTEQ, can calculate pE or Eh based on measured concentrations of DO and other chemical species subject to redox reactions.

Other Variables Affecting Solubility

The concentration of other solutes in water affects solubility, with high concentrations of other solutes reducing the effective ability of the solution to dissolve a newly introduced solute (for example, a soluble mineral along a seepage flow path). Temperature and pressure affect solubility. Generally, the solubility of electrolytes and solid nonelectrolytes increases with higher temperature, while the solubility of gases decreases at higher temperature. Pressure greatly affects gas solubility, but in the upper 300 m of earth surface where dam seepage occurs, the solubility of solid minerals in water is relatively unaffected by increased pressure from the weight of soil and rock overburden at depth.

Solubility Data and the Real World

The theory underlying the chemistry of solubility and dissolution assumes conditions that are often not present in the dynamic real world environment of seepage. This section discusses the chemical equilibrium concept derived from thermodynamics, how the changing conditions and complexity of seepage violate the theoretical assumptions of thermodynamics, and how meaningful information regarding mineral dissolution at dams can be obtained despite assumption violations.

The Equilibrium Concept and Solubility Classes

Solubility data are reported for many different minerals; however, these data require some clarification. First, these values usually assume *equilibrium* conditions between a single solute and pure deionized water (di H_2O), and only refer to a single reaction, such as:

$$\underset{\textit{halite}}{NaCl} \xrightarrow{H_2O} Na^+ + Cl^- \qquad \text{Eq. 3}$$

Equilibrium conditions exist only when the system is *closed* (no net flux of energy or mass into or out of the system), the system is at constant temperature and pressure, and the rate of the reaction does not matter. Thermodynamics, which describes the ultimate stability of chemical compounds, does not consider the rates of reactions (called *kinetics*). Equilibrium assumptions are often violated in the dynamic reservoir seepage environment where conditions vary with changing physical, hydraulic, and chemical energy inputs and outputs during the reservoir hydrologic cycle. So, shorter seepage transit times may mean that the mineral is effectively less soluble than solubility data suggest.

Solubility is usually defined as the maximum amount of a solute mineral, expressed in mass per unit volume, that can dissolve at a given temperature (usually 25 °C) in di H_2O. Below this amount of solute, the solution is called *undersaturated*. If solute is added over and above this amount, it remains as a solid phase with the liquid and does not dissolve into solution. When solid solute coexists with liquid solution, it is called a *saturated solution*. Under certain conditions, a solution may contain more solute than the solubility limit suggests, called a *supersaturated* or *oversaturated* solution. Given time, however, a solute usually *precipitates* (forms the solid compound) out of an oversaturated solution.

The solubility of a mineral also declines as the concentration in the solvent water increases. Reservoir water contains previously dissolved cations, anions, and other trace inorganic and organic compounds, and water having higher concentrations of solutes is less able to dissolve minerals during seepage transit. Reservoir water also becomes more concentrated as it flows beneath the dam and dissolves minerals, so seepage water can become less aggressive dissolving minerals toward the end of its transit. Concentrations of reservoir water also vary with season and depth because of thermal and chemical stratification. During

winter and summer, when deeper reservoirs stratify, higher concentration water sinks to the bottom where seepage often begins its underground transit through the foundation or abutments.

Seepage flow beneath a dam fluctuates depending on reservoir surface elevation, so seepage residence time varies during the year. Some dissolution reactions are fast, but many involving minerals are slow and can be hindered by hydrodynamic factors. Varying degrees of water-mineral contact and mixing (or lack of mixing) also occur during seepage transit. The kinetics of dissolution reactions can also affect the formation rates of voids and flow channels (Dreybrodt, 1988; James and Kirkpatrick, 1980; Ford and Ewers, 1978). In a dam, the seepage flow paths and dissolution rates may change over time as more readily soluble minerals are depleted, void spaces and new flow paths form, and mineral dissolution becomes mechanical erosion.

Despite equilibrium assumption violations, solubility data do give us an idea of the *relative* differences in solubility between minerals. Soluble classes of minerals are defined here as:

- *Very soluble*.—Solubilities on the order of 10 to >100 g/L. These minerals are usually called *evaporites* because they formed sediments as paleo-ocean and -lake waters evaporated. They are usually associated with sedimentary deposits and artesian hydrothermal springs in volcanic geology. Examples include the minerals halite (sodium chloride, NaCl), thenardite (anhydrous sodium sulfate, Na_2SO_4), mirabilite (sodium sulfate decahydrate, $Na_2SO_4 \cdot 10H_2O$), natron (sodium carbonate decahydrate, $Na_2CO_3 \cdot 10H_2O$), and borax (sodium borate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$).

- *Soluble*.—Solubilities on the order of 0.5 to 10 g/L (500 to 10,000 mg/L). These minerals may be evaporites or precipitates. Examples include gypsum (calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$), anhydrite (anhydrous calcium sulfate, $CaSO_4$), and villiaumite (sodium fluoride, NaF).

- *Sparingly soluble*.—Solubilities on the order of 0.001 g/L to 0.50 g/L (1 to 500 mg/L). Examples include calcite (calcium carbonate, $CaCO_3$), dolomite (calcium-magnesium carbonate, $(Ca,Mg(CO_3)_2)$), magnesite (magnesium carbonate, $MgCO_3$), and amorphous silica (silicon dioxide, SiO_2).

Summary of Chemistry Concepts

Solubility occurs when electrolytes, such as simple minerals, dissociate into dissolved ions, or nonelectrolytes become hydrated and thus become stable in solution. The most important factors affecting the solubility of minerals are pH and redox potential. Temperature, pressure, and the concentration of water also affect mineral solubility to a lesser degree. Solubility data for minerals listed in reference tables are based on equilibrium assumptions that are often violated in seepage and mineral dissolution. Despite these assumption violations, we can classify minerals into broad classes of solubility: very soluble, soluble, sparingly soluble, and insoluble.

- *Insoluble*.—Solubilities on the order of <0.001 g/L (1 mg/L). Examples include more complex classes of silicate and aluminosilicate minerals such as the rock-forming minerals diopside ($CaMgSi_2O_6$), hornblende ($Ca_2Mg_4AlSi_7O_{22}(OH)_2$), and orthoclase feldspar ($2KAlSi_3O_8$), clays such as calcium montmorillionite ($Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2$), and crystalline silica minerals such as quartz (SiO_2).

In general, the more complex a mineral, the less soluble it is. Table 1 provides a summary of published solubilities and densities for typical minerals in each of the different solubility classes used in this report (Barthelmy, 2004; Budavari, et al., 1996; Seelig, 2000; Winkler, 1975).

Weathering and Geochemistry

This section reviews some of the geology concepts associated with mineral weathering and dissolution, and how these processes affect water quality and mineral dissolution.

Weathering and Mineral Dissolution

In geology, the breakdown and transformation of rocks and minerals by exposure to the atmosphere, water, wind, and light is called *weathering*. Mountains, whether volcanic or metamorphic in origin, usually contain crystalline feldspars and silica. The general weathering sequence for exposed rocks is for the relatively simple, lower-molecular weight, and crystalline feldspars and quartz minerals to slowly break down, liberating free ions that may dissolve into surface waters and also form other minerals such as clays. A good example is the Denver Basin, which is composed of clay and claystones that formed from the weathering of the nearby granitic and crystaline Rocky Mountains.

Snowmelt and rain in upper elevation watershed reaches are essentially di H_2O in equilibrium with the atmosphere. Almost as soon as the water begins flowing downhill, however, it begins to erode, dissolve, and alter rocks, and thereby increases the concentrations of solutes in water. At lower elevations, sedimentary deposits containing greater amounts of soluble minerals are exposed, and these solutes also dissolve as water flows down gradient. In dam seepage, we are primarily concerned with aspects of weathering involving seepage water dissolving or partially breaking down salts and simple minerals from soils and sedimentary rock close to the dam. There are two primary weathering processes that affect minerals and seepage: congruent and incongruent dissolution.

Table 1.—Reported aqueous solubilities and densities for some simple and complex minerals arranged by solubility class. Values are from several sources and represent generally neutral pH water as the solvent (Hem, 1992; Budavari et al.,1996; Barthelmy, 2004; Winkler, 1975; Seelig, 2000; Deer, et al., 1992)

Solubility class	Mineral name or class	Chemical name or example minerals	Chemical formula	Solubility, g/L	Density, g/cm^3
Very soluble	Antarcticite	Calcium chloride hexahydrate	$CaCl_2 \bullet 6H_2O$	1,620	1.71
	Bischofite	Magnesium chloride hexahydrate	$MgCl_2 \bullet 6H_2O$	1,190	1.56
	Hexahydrite	Magnesium sulfate hexahydrate	$MgSO_4 \bullet 6H_2O$	948	1.76
	Epsomite	Magnesium sulfate septahydrate	$MgSO_4 \bullet 7H_2O$	757	1.67
	Mirabilite	Sodium sulfate decahydrate	$Na_2SO_4 \bullet 10H_2O$	670	1.46
	Natron (washing soda)	Sodium carbonate decahydrate	$Na_2CO_3 \bullet 10H_2O$	500	1.46
	Thenardite	Anhydrous sodium sulfate	Na_2SO_4	388	2.68
	Halite	Sodium chloride	$NaCl$	360	2.17
	Sylvite	Potassium chloride	KCl	360	1.98
	Oakite	Sodium phosphate dodecahydrate	$Na_3PO_4 \bullet 12H_2O$	280	1.60
	Trona (baking soda)	Sodium bicarbonate-carbonate dihydrate	$Na_3(HCO_3)CO_3 \bullet 2(H_2O)$	100	2.13
	Borax	Sodium borate decahydrate	$Na_2B_4O_7 \bullet 10H_2O$	62.5	1.73
Soluble	Villiaumite	Sodium fluoride	NaF	4.3	2.78
	Gypsum	Calcium sulfate dihydrate	$CaSO_4 \bullet 2H_2O$	2.4	2.3
	Anhydrite	Anhydrous calcium sulfate	$CaSO_4$	2.1	2.97
Sparingly soluble	Magnesite	Magnesium carbonate	$MgCO_3$	0.084	3.00
	Dolomite	Calcium-magnesium carbonate	$(Ca,Mg)(CO_3)_2$	0.050	2.84
	Calcite	Calcium carbonate	$CaCO_3$	0.014	2.71
	Amorphous Silica	Silicon dioxide	SiO_2	0.030-0.100	2.10 (opal)
Insoluble	Diopsides	Diopside, hedenbergite	$Ca(Mg,Fe)[Si_2O_6]$	-	3.22-3.56
	Chlorites	Brucite, gibbsite	$(Mg,Fe,Mn,Al)_{12}[(Si,Al)_8O_{20}](OH)_{16}$	-	2.6-3.3
	Hornblendes	Pargasite, edenite	$Ca_2(Mg,Fe)_4AlSi_7AlO_{22}(OH)_2$	-	3.02-3.59
	Alkali feldspars	Microcline, sanidine	$(K, Na)[AlSi_3O_8]$	-	2.55-2.63
	Plagioclase	Albite, anorthite	$Na[AlSi_3O_8]$-$Ca[AlSi_3O_8]$	-	2.62-2.76
	Crystalline silica	Quartz, cristobalite	SiO_2	-	2.26-2.65
	Clays	Smectites: $(Ca,Na_2)_{0.7}(Al,Mg,Fe)_4[(Si,Al)_8O_{20}](OH)_4 \bullet nH_2O$ Kaolinites: $Al_4[Si_4O_{10}](OH)_8$ Illites: $K_{(1.5-1.0)}Al_4[Si_{(6.5-7.0)}Al_{(1.5-1.0)}O_{20}](OH)_4$		- - -	2-3 2.61-2.68 2.6-2.9

Congruent Dissolution

Congruent dissolution is a straightforward aqueous dissolution of a relatively simple mineral, such as halite, into its constituent sodium and chloride ions (equation 1). Because congruent dissolution represents a complete breakdown of the mineral, it also produces structural voids where the soluble minerals were located. The most important congruent reactions are those involving soluble sulfate minerals gypsum and anhydrite:

$$\overset{\textit{Gypsum}}{CaSO_4 \cdot 2H_2O} \rightleftharpoons \overset{\textit{Calcium ion}}{Ca^{2+}} + \overset{\textit{Sulfate ion}}{SO_4^{2-}} + 2H_2O \qquad \text{Eq. 4a}$$

$$\overset{\textit{Anhydrite}}{CaSO_4} \rightleftharpoons \overset{\textit{Calcium ion}}{Ca^{2+}} + \overset{\textit{Sulfate ion}}{SO_4^{2-}} \qquad \text{Eq. 4b}$$

and the limestone-associated carbonate minerals calcite, magnesite, and dolomite:

$$\overset{\textit{Calcite}}{CaCO_3} + H_2O + CO_2 \rightleftharpoons Ca^{2+} + \overset{\textit{Bicarbonate ion}}{2HCO_3^-} \qquad \text{Eq. 5a}$$

$$\overset{\textit{Magnesite}}{MgCO_3} + H_2O + CO_2 \rightleftharpoons Mg^{2+} + \overset{\textit{Bicarbonate ion}}{2HCO_3^-} \qquad \text{Eq. 5b}$$

$$\overset{\textit{Dolomite}}{CaMg(CO_3)_2} + H_2O + CO_2 \rightleftharpoons Ca^{2+} + Mg^{2+} + \overset{\textit{Bicarbonate ion}}{2HCO_3^-} \qquad \text{Eq. 5c}$$

Dam safety professionals should be concerned with these congruent reactions because of the extensive presence of limestone and sedimentary evaporite deposits in the western United States, and the structural risk posed by void formation in the abutments and foundations of dams. All of the above congruent mineral reactions produce voids.

Void formation risks are exacerbated when the geology structurally supporting dams includes limestone and gypsum in *karst* terrains. Abutment or foundations composed of karst or containing evaporite deposits can potentially have very high permeability due to fracturing and previously formed void spaces, and must often be grouted. Worldwide, most of the dams having structural problems caused by mineral dissolution have foundations and abutments located in karstic geology containing calcite and gypsum deposits (James and Lupton, 1978; James and Kirkpatrick, 1980; James, 1981; James, 1985). Calcite and silica can also be present as cementing agents in sandstones, mudstones, and shales, so seepage may increase abutment or foundation permeability over time (on the order of decades) even when these sparingly soluble minerals will not form large void spaces.

Most congruent dissolution involves minerals from the very soluble to sparingly soluble classes; however, some insoluble class minerals, such as chlorites or pyroxenes, may also undergo congruent dissolution under special conditions (such

as acidic conditions in exposed rocks at upper elevations) (Loughnan, 1969). However, these reactions contribute very little to seepage concentration increases:

$$\underset{\textit{Chlorite}}{Mg_5Al_2Si_3O_{10}(OH)_8} + 10H_2O \rightleftharpoons \underset{\textit{Magnesium ion}}{5Mg^{2+}} + 2Al(OH)_4^- + 3H_4SiO_4 + 8OH^- \quad \text{Eq. 6}$$

Incongruent Dissolution

Incongruent dissolution occurs when one mineral transforms into another mineral, in the process producing some constituent ions that may increase (or decrease) seepage concentrations. These weathering reactions are common, but may be very slow relative to seepage residence times in a dam structure, and thus cannot contribute significantly to solute increases in seepage (Clayton, 1986). Potassium feldspar (orthoclase) weathering to form the clay kaolinite is an example of incongruent dissolution (Loughnan, 1969; Drever, 1988):

$$\underset{\substack{\textit{K-feldspar}\\ \textit{(orthoclase)}}}{2KAlSi_3O_8} + 11H_2O + 2CO_2 \rightleftharpoons \underset{\textit{Kaolinite}}{Al_2Si_2O_5(OH)_4} + 2K^+ + 2HCO_3^- + 4H_4SiO_4 \quad \text{Eq. 7}$$

which produces bicarbonate and silica (as H_4SiO_4) as reaction byproducts. Kaolinite can then undergo incongruent dissolution to form a smectite clay, montmorillonite, by *depleting* hydrated SiO_2 and Ca^{2+} (Drever, 1988):

$$\underset{\textit{Kaolinite}}{7Al_2Si_2O_5(OH)_4} + \underset{\textit{Hydrated Silica}}{8H_4SiO_4} + Ca^{2+} \rightleftharpoons \underset{\textit{Ca-Montmorillonite}}{6Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2} + 23H_2O + 2H^+ \quad \text{Eq. 8}$$

Incongruent dissolution may increase or decrease ion concentrations (notably HCO_3^-, Al, and SiO_2) in seepage; however, its contribution to seepage concentration increases is usually on the order of less than 3 percent of total change in concentration. In some cases, an incongruent mineral reaction may actually reduce the amount of particular reactants, as seen for H_4SiO_4 and Ca^{2+} in equation 8.

The formation of void spaces from incongruent dissolution is also a complex issue. Depending on the densities of the parent and weathered minerals, swelling and reduction of seepage flow may also occur. See appendix 3 for examples of void formation and mass wasting calculations and precautions.

Mineral dissolution is a complex process that varies within in a given structural location, sedimentary unit, and flowpath geology, and both congruent and incongruent dissolution processes are likely to occur.

Weathering and Water Quality

Mineral weathering is a major process affecting water quality. Water quality is a general term that is actually referring to the *quantity* of chemical compounds and constituents in water. Good water quality usually means low concentrations of chemicals, while poor water quality usually means high concentrations, or water containing toxic compounds. In seepage chemistry investigations, we need to focus on two general classes of chemical components that comprise what we call water quality: the major ions, and trace and ultratrace constituents.

The Major Ions

The dominant constituents in natural waters produced by weathering are known as the *major ions*. These solutes include the positive ions (cations) calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}) and potassium (K^{+}); and the negative ions (anions) carbonate (CO_3^{2-}), bicarbonate (HCO_3^{-}), sulfate (SO_4^{2-}), and chloride (Cl^{-}). In most natural waters, CO_3^{2-} and HCO_3^{-} comprise what is called alkalinity. Alkalinity can be thought of as the acid-neutralizing ability of water, and includes hydroxide ion (OH^{-}) for waters with elevated pH (such as those contacting grout or cement). The major ions usually occur in the range of many milligrams per liter (mg/L) or milliequivalents per liter (meq/L) concentration and comprise what is usually referred to as general water quality. Table 2 provides molecular and equivalent weights for the major ions.

Table 2.—Molecular and equivalent weights and equivalent conductivities for the major ions. To calculate meq/L, divide concentration in mg/L by the equivalent weight.

Ion/compound name	Chemical formula	Molecular weight, mg/mMole	Equivalent weight, mg/meq	Equivalent conductivity, µS/cm per mg/L
Carbonate	CO_3^{2-}	60.0094	30.0047	2.82
Bicarbonate	HCO_3^{-}	61.0171	61.0171	0.715
Hydroxide	OH^{-}	17.0073	17.0073	5.56
Calcium carbonate	$CaCO_3$	100.0874	50.0437	not applicable
Sulfate	SO_4^{2-}	96.0636	48.0318	1.54
Chloride	Cl^{-}	35.4527	35.4527	2.14
Calcium	Ca^{2+}	40.078	20.039	2.60
Magnesium	Mg^{2+}	24.3050	12.1525	3.82
Sodium	Na^{+}	22.9898	22.9898	2.13
Potassium	K^{+}	39.0983	39.0983	1.84

Trace and Ultratrace Constituents

Besides the major ions, trace constituents (at concentrations around 1 mg/L and less) are also produced by mineral weathering, including silica (SiO_2, present in water as H_4SiO_4), strontium (Sr), boron (B, present in water as borate ion, $B_4O_7^{2-}$), fluoride (F^-), bromide, (Br^-), phosphorus (P, present in water as phosphate ion, PO_4^{3-}), and trace elements such as iron (Fe), manganese (Mn), aluminum (Al), and barium (Ba). Weathering also contributes all the microgram per liter (μg/L) ultratrace elements, such as mercury (Hg), cadmium (Cd), zinc (Zn), copper (Cu), lead (Pb), selenium (Se), arsenic (As), and many others.

Nitrogen (N), organic carbon (OC), and phosphorus (P) are important trace constituents usually associated with the byproducts of living systems in watersheds, and these constituents are also present at μg/L to mg/L levels in surface waters. Organic carbon enters surface water from watershed plant and animal decay in runoff as humic and fulvic materials: a complex assemblage of various molecular weight organic acids and other compounds that originally were proteins, carbohydrates, and lipids in living systems. As the OC breaks down further, N and P are also released into water (Thurman, 1985).

Describing Water Quality

Often, water quality is summarized as the sum of dissolved constituents, called total dissolved solids (TDS) (Hem, 1995). TDS is measured in mg/L by evaporating known volumes of a water and then weighing the residue. In many waters, the sum of the individual major ions in mg/L approximates the TDS by evaporation. TDS generally increases as elevation decreases and water has been in contact with greater amounts of soil and rock for longer periods of time. In upper elevation waters (higher than 3,000 m, or 9,800 ft), TDS can vary from less than 20 to 100 mg/L. In lower elevation waters, such as Lake Powell (elevation approximately 3,500 ft, or 1,070 m), TDS ranges from 500 to 1,000 mg/L.

Another useful variable describing the overall concentration of waters is electrical conductivity, EC, measured in microSiemens per centimeter (μS/cm). Waters containing dissolved electrolytes conduct electricity in proportion to concentration; however, as water becomes more concentrated, charged electrolytes in solution tend to form ion pairs

Summary of Weathering and Geochemistry

Weathering is the overall process whereby rainwater dissolves and converts minerals, creating the major ions and trace compound solutes that are collectively known as water quality constituents. The two important classes of mineral weathering are congruent (complete) and incongruent (partial) dissolution, and both contribute major ions and trace constituents to water. Changes in water quality between reservoir water and seepage can be easily visualized using multivariable polygon plots such as Stiff and radar diagrams. For more detailed information, refer to Drever's text, *The Geochemistry of Natural Waters* (1988), Hem's *Study and Interpretation of the Chemical Charactistics of Natural Water* (1992), or Stumm and Morgan's *Aquatic Chemistry* (1996), all of which are widely respected technical references.

that do not contribute to EC. Thus, the relationship between EC and ion concentration is not linear. Generally, EC in µS/cm approximates TDS and sum of ions in mg/L, and can be used to check overall analysis quality (APHA-AWWA-WEF, 1998).

A good way to visualize major ions and trace concentration data is to use polygon plots, such as Stiff (Stiff, 1951), Piper (Piper, 1944), and radar diagrams, seen in figure 1. These plots are a simple and helpful way to visualize many variables at the same time and to recognize similar chemistry by the size and shape of polygons, and will be seen again in the *Interpreting Seepage Chemistry and Mineral Dissolution* section below.

Other Processes Affecting Seepage Chemistry

Just because seepage chemistry concentrations are higher than reservoir concentrations does not automatically imply mineral dissolution, even in a structure where gypsum and calcite are present. A careful evaluation must consider biotic (bacterial) processes, ion exchange on clays, mixing of different groundwaters, and delayed seepage of higher concentration reservoir water. It is important that these other processes are carefully evaluated in order to avoid alarmist conclusions regarding void formation from mineral dissolution.

Biotic Processes

Water quality is strongly affected and changed by living microorganisms that use carbon and oxygen (Redfield, et al.,1963).

Metabolism and Respiration

Almost all living things must assimilate or burn carbon (growth and metabolism), and breathe oxygen (respiration), and these reactions also change the concentrations of several of the major ions in water (Atlas and Bartha, 1998; Manahan, 1994). Surface waters usually contain DO from algal photosynthesis and atmospheric mixing, and organic carbon (OC) from plant and animal decay that fluctuate in a dynamic steady state. These materials form the culture medium for bacteria, algae and other microorganisms at the base of the aquatic food chain. Reservoirs with elevated OC and high primary productivity (*eutrophic* systems) form a richer culture medium for bacteria compared to lower productivity reservoirs (*oligotrophic* systems).

Surface waters mixed with the atmosphere have a constant source of fresh O_2, but underground as seepage, bacteria gradually deplete the supply of DO during seepage transit (Bitton and Gerba, 1984; Domenico and Schwartz, 1990). The

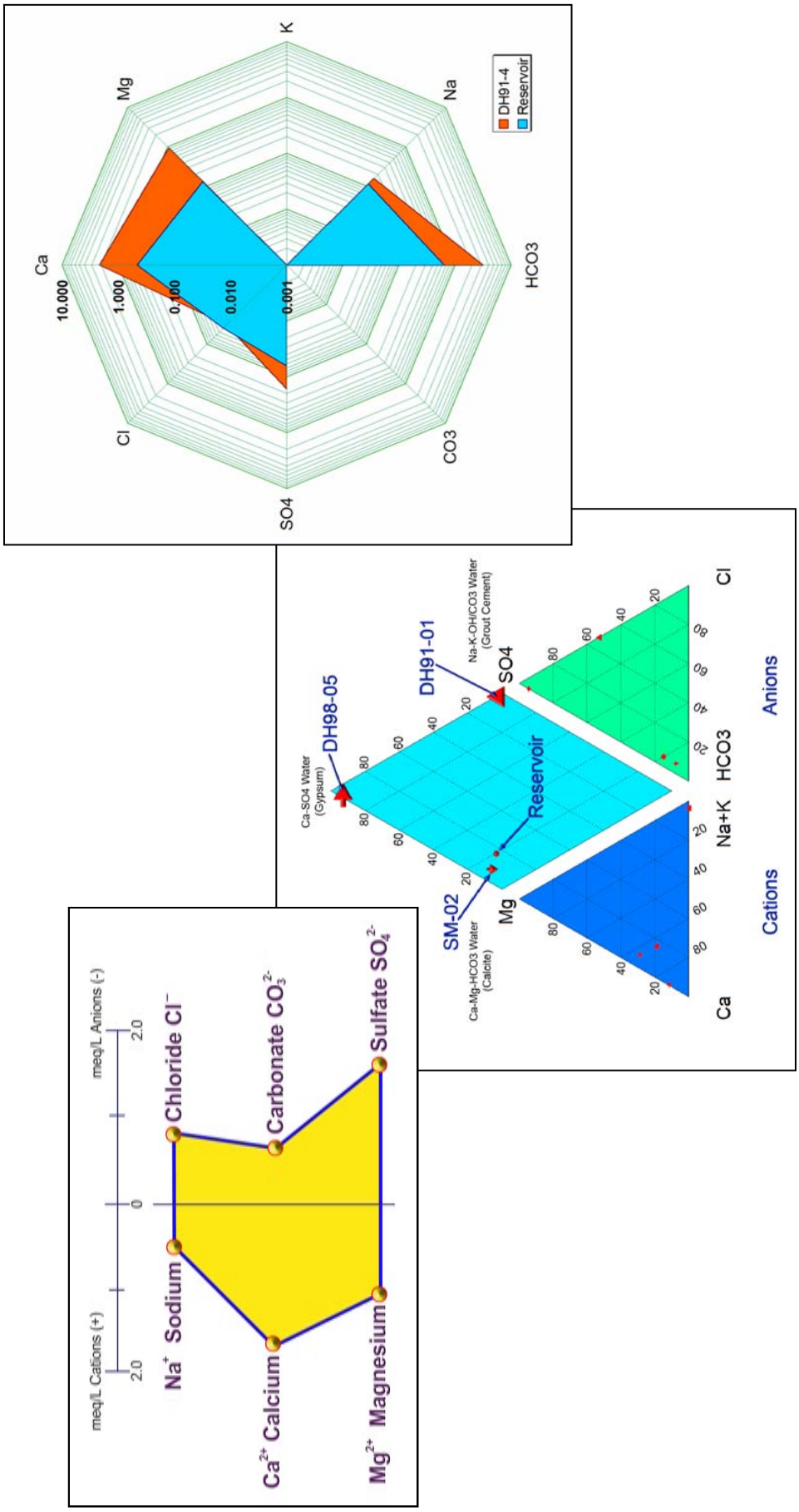

Figure 1.—Polygon plots are helpful ways to visualize seepage water major ions chemistry data. Above left is a Stiff diagram (Stiff, 1951) that plots cations to the left and anions to the right. To the right is a radar diagram created in a Microsoft Excel® spreadsheet that plots all the major ions on a logarithmic scale with 0.001 meq/L at the center. Piper diagrams (above center) plot major ions data and are used to classify the geochemical type of seepage water.

general reaction for the bacterial oxidation (breakdown or metabolism) of organic carbon is (Drever, 1988; Thurman, 1985):

$$\overset{\textit{organic carbon}}{CH_{2.48}O_{1.04}N_{0.151}P_{0.0094}} + 1.3O_2 + H_2O \rightarrow HCO_3^- + \overset{\textit{nitrate}}{0.151NO_3^-} + \overset{\textit{phosphate}}{0.0094HPO_4^{2-}} + 1.15H_2O + 1.17H^+ \quad \text{Eq. 9}$$

For each organic carbon molecule, 1.3 molecules of O_2 are reduced, forming HCO_3^- (an aqueous proxy for CO_2). Besides HCO_3^-, the byproducts of this reaction include some nitrate (NO_3^-), phosphate (PO_4^{3-}), and some acidity (H^+). So, measurement of changes in OC, DO, pH, NO_3^-, and PO_4^{3-} between reservoir and emergent seepage can be indicative of relative seepage residence time and biotic processes during transit. Table 3 shows lower dissolved OC (DOC) concentrations in seeps and weirs compared to reservoir samples measured at Deer Flat Embankments, Caldwell, Idaho (Craft, 1989), showing measurable changes in OC, suggesting that biotic processes are likely.

Table 3.—DOC concentrations (mg/L as C) measured in Lake Lowell and seeps at Deer Flat Embankments. The reservoir is shallow and very eutrophic and so promotes bacterial activity in seepage where OC is metabolized.

Sample location	TOC, mg/L	DOC, mg/L
Reservoir at lower embankment	> 8.0	3.8
Weir 4	1.7	1.7
Natural conduit	1.4	1.4
Reservoir at upper embankment	6.0	3.0
Weir 12	1.2	1.2
Manhole	1.8	1.8

The Sequence of Bacterial Activity

When seepage begins its underground transit, bacteria begin to change redox conditions in a predictable manner. First, aerobic and facultative bacteria species (bridge species able to respire under both aerobic and anaerobic conditions) deplete the available DO. Then a sequence of facultative bacteria followed by anaerobic species begin chemically reducing other oxygen-containing compounds in order to continue metabolizing food carbon.

This process proceeds with oxygen-containing compounds requiring less energy to reduce being depleted first. Once one source of oxygen is depleted, a different bacteria species begins to dominate until the next available oxygen compound depleted through reduction. At each stage, the system becomes more reducing and measured Eh becomes increasingly negative. In groundwaters and seepage (as well as bottom waters in stratified lakes), the sequence of bacterial

respiration/reduction proceeds as follows (Gunnison and Brannon, 1981; Stumm and Morgan, 1994; Drever, 1988; Atlas and Bartha, 1998):

1. *DO depletion*.—Aerobic bacteria such as *Micrococcus, Pseudomonas, and Nocardia* metabolize OC and respire DO, depleting the supply in water. In surface waters, algal photosynthesis and atmospheric mixing replenishes DO, but seepage experiences DO depletion as soon as it becomes groundwater. The reaction for aerobic oxidation of OC and reduction of O_2 is seen in equation 9. Eh values are positive whenever any DO is present; however, platinum electrode measurements in oxygenated waters are not indicative of the true pE of the system.

2. *Nitrate (NO_3^-) depletion and denitrification*.—In unpolluted oxygenated waters, NO_3^- is formed from the bacterial oxidation (by *Nitrosomonas* and *Nitrobacter*) of ammonia (NH_3, N in the -III oxidation state) derived from the breakdown of proteins and amino acids from the decay of dead organisms. Once DO is depleted, oxygen in NO_3^- (N in the +V oxidation state) is respired and reduced to nitrite (NO_2^-, N in the +III oxidation state) by bacteria such as *Aeromonas, Enterobacter,* and *Acaligenes* (Manahan, 1994; Atlas and Bartha, 1998):

   $$NO_3^- + 0.50C_{organic} \rightarrow NO_2^- + 0.50H_2O + 0.50CO_2 \qquad \text{Eq. 10}$$

   Denitrification occurs under anaerobic conditions mediated by bacteria such as *Paracoccus denitrificans,* or *Thiobacillus denitrificans*. This process involves the complete reduction of NO_3^- to N_2 gas (N in the 0 oxidation state) by way of several intermediary oxidation states (NO (+II), N_2O (+I)). If seepage is near the surface, the N_2 gas may leave the aqueous solution and return to the atmosphere (Manahan, 1994; Atlas and Bartha, 1998):

   $$0.20NO_3^- + 0.25C_{organic} + 0.25H^+ \rightarrow 0.10N_2 + 0.35H_2O + 0.25CO_2 \qquad \text{Eq. 11}$$

   Eh values for nitrate reduction range from 0 to -100 mV.

3. *Reduction of Mn- and Fe-oxyhydrates*.— Fe and Mn are common and important trace elements that regulate many adsorption reactions of other water quality constituents in natural waters. In oxygenated waters, both Fe and Mn form insoluble ferric (Fe^{3+}) and manganic (Mn^{+4}) ions that readily combine with oxygen and hydroxide to form what are called oxyhydrates. Heterogeneous assemblages of compounds such as $Fe(OH)_3$, FeOOH, or MnO_2, readily adsorb onto suspended particulate matter and form adsorptive surfaces that attract other trace elements, organic matter, and also bacteria such as *Bacillus, Pseudomonas,* and *Proteus*. Once DO and NO_3^- have been depleted, these bacteria can respire oxyhydrate-O by reducing Fe^{3+} and Mn^{+4} (Myers and Nealson, 1988; Manahan, 1994). Typical Eh values for Fe and Mn reduction are around -50 to -200 mV.

$$FeOOH + C_{organic} \rightarrow Fe^{2+} + CO_2 + H^+ \qquad \text{Eq. 12}$$

$$MnO_2 + C_{organic} \rightarrow Mn^{2+} + CO_2 \qquad \text{Eq. 13}$$

4. *Reduction of sulfate to sulfide*.—Once Fe and Mn reducing bacteria deplete the available supplies of O in oxyhydrates, sulfate reducing bacteria begin to increase in numbers. Species such as *Desulfovibrio, Desulfotomaculum,* and *Desulfobacter* create hydrogen sulfide (H_2S) gas, the rotten egg odor smelled in stagnant wells and deep lake sediments exposed to the atmosphere. Eh values range from -200 to -300 mV, usually the most severe reducing conditions seen in dam seepage.

$$SO_4^{2-} + 2C_{organic} + 2H_2O \rightarrow H_2S_{(g)} + 2HCO_3^- \qquad \text{Eq. 14}$$

5. *Methanogenesis—CO_2 reduction to methane, CH_4*.—After the sulfate reduction process is exhausted, methanogens, a distinct group of Archaea microbes (such as *Methanobacterium*), begin to utilize C from CO_2 and HCO_3^- to produce CH_4. This process relies on fermentation, rather than respiration, and is strictly anaerobic. Methanogens produce the most severe reducing conditions possible in natural waters. Eh values range from -350 to -450 mV, and such severe conditions are only rarely found in dam seepage.

$$HCO_3^- + H^+ + 4H_2 \rightarrow CH_{4(g)} + 3H_2O \qquad \text{Eq. 15}$$

So, biotic processes contribute more to concentration increases with longer seepage residence times and adequate substrate for metabolism and respiration. Investigations at Deer Flat Embankments revealed that around half of the observed increases in seepage concentrations were caused by biotic processes, not mineral dissolution. This should not be surprising since Lake Lowell is a shallow eutrophic reservoir that is home to large populations of waterfowl. The water contains elevated OC from seeping through a thick coating of organic muck and reducing sediments before entering the embankment foundations (Craft, 1989).

Ion Exchange

Mountains containing metamorphic and volcanic feldspars and silica eventually weather to form sediments including clays and clay minerals (Deer, et al., 1992). In the West, clay minerals collect in valleys and basins from water runoff, but can also accumulate in deposits from glaciers (as moraines) and wind transport (eolian deposits, or loess). Clay minerals, usually smectites and illites, constitute most of the upper surface layers of basin soils, and are also used as embankment materials in earthen dams because of their low permeability when compacted.

Clay minerals are sheetlike aluminosilicates that can form layers loosely held together by Ca, Mg, Na, and K ions (Deer, et al., 1992; Borchardt, 1977). These interlayer cations are not strongly bound, and experience a reaction called *ion*

exchange. If the influent seepage water contacting clays contains larger proportions of Ca compared to Na, Ca can exchange for Na in the clay lattice (in a Na-montmorillionite, for example), and thus increase Na concentration (and decrease Ca) in the seepage water (Kelly, 1948; Lindsay, 1979).

$$Na^{+} + \underbrace{Ca_{0.5}Al_{6.85}Si_{10.8}O_{29.4}(OH)_{5.88}}_{\textit{Ca-Montmorillonite}} \rightleftharpoons \underbrace{NaAl_{6.85}Si_{10.8}O_{29.4}(OH)_{5.88}}_{\textit{Na-Montmorillonite}} + 0.5Ca^{2+} \quad \text{Eq. 16}$$

Mixing and Hydrologic Factors

The last factor affecting seepage chemistry to consider at dams involves hydrologic variables affecting the mechanical movement of seepage water near the dam, and the mixing of local seepage water types.

Mixing with Another Groundwater Aquifer

Usually, we think of dam seepage as being dominated by the hydraulic head of the reservoir forcing reservoir water around and through geologic materials in the abutments, foundation, and embankment. In many cases, this assumption is probably valid; however, mixing with older *connate* groundwater should also be considered. Rivers are natural groundwater discharge zones (Freeze and Cherry, 1979; Heath, 1989), and the groundwater aquifer that existed prior to the dam and reservoir may continue to seep into and mix with reservoir-derived seepage. Figure 2a shows how this mixing might occur.

The only way to know whether this is happening at a site is to collect and analyze groundwater samples from observation wells located away from the dam and the reservoir seepage influence zone, and to then compare the connate groundwater data to reservoir and seepage chemistry data (Quinlin, 1992; Barcelona, et al., 1985). Various mixing programs, such as NETPATH (Plummer, et al., 1991), may be used with major ions data to corroborate whether seepage chemistry is the plausible result of mixing of reservoir and groundwater sources. Another approach to identify connate groundwaters is to determine the abundance of isotopes ^{2}H, ^{13}C, ^{18}O, ^{15}N, and ^{34}S using stable isotope ratio mass spectrometry. Recent surface waters and different groundwaters have varying ratios of the stable isotopes that may be used to identify and distinguish different sources, mixing ratios, and even seepage flow rate and residence time (Kaufmann, et al., 1953; Eggenkamp, et al., 1998.; Desaulniers, et al., 1986; Long, et al., 1993).

Local Mixing along Seepage Flow Paths

Another kind of mixing is more localized along seepage flow paths, and can be related to diffusion between adjacent sedimentary layers of different mineralogy and permeability along seepage flow paths. Some of the higher concentration water may naturally diffuse from high concentration layers to lower concentration seepage flows, increasing the seepage concentrations. Water in a relatively stagnant toe drain, for example, may mix with faster flowing, lower concentration seepage underneath the toe. Another example could be a layer with low

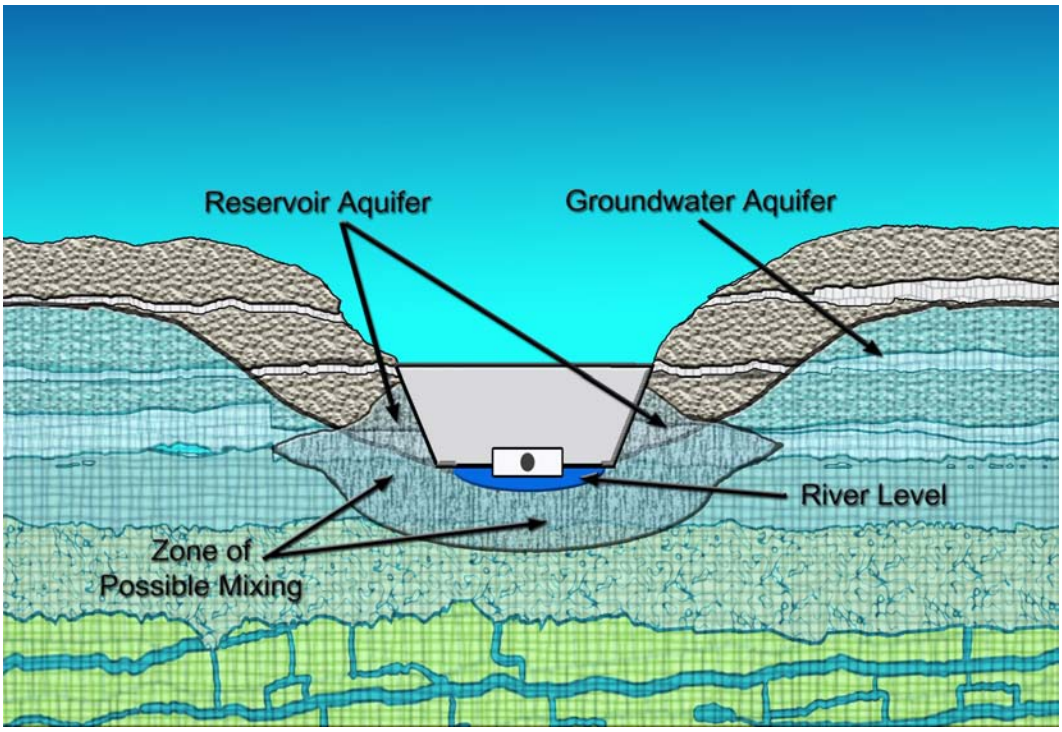

Figure 2a.—A downstream view of a dam (looking upstream at the dam) showing a hypothetical mixing scenario between the local reservoir-dominated seepage aquifer and the previously existing groundwater aquifer.

permeability and long seepage residence (perhaps a shale) that may have higher concentration seepage compared to an adjacent karst layer containing voids and calcite with higher permeability and flow. Figure 2b shows how this process might occur.

Changing Reservoir Water Quality and Delayed Flows

Finally, delayed flow of seepage around the abutments of a dam may account for increases in seepage concentrations. At Glen Canyon Dam, public advocacy groups expressed concern about potential mineral dissolution when seepage emerging at a downstream canyon wall was seen with elevated concentrations compared to reservoir surface samples from the same date. A study of seepage at Glen Canyon Dam (Craft, 1991) using the MODFLOW groundwater flow model (McDonald and Harbaugh, 1988) revealed that seepage flowed horizontally around the dam and had estimated residence times of around 6 months. Additionally, Lake Powell, which varies between 350 to 500 feet in depth behind the dam, experiences both thermal and chemical stratification, with bottom (hypolimnetic) major ions concentrations often 25 percent greater than surface (epilimnetic) concentrations. This study suggested that the seep of concern actually contained higher concentration reservoir water seeping from deep below the chemocline and delayed by natural semicircular horizontal flow around the abutment (fig. 2c).

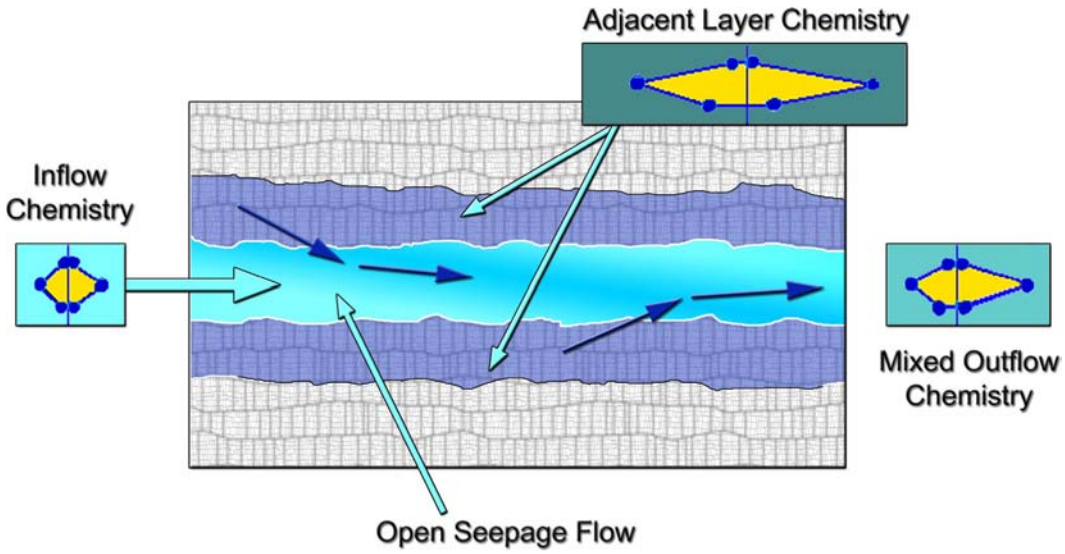

Figure 2b.—A cross section of subsurface rock showing a mixing scenario between an open seepage flow and higher concentration water in adjacent low permeability strata. Seepage flow is from left to right. Stiff diagrams are used to show the chemistry of the different waters and the resulting mixture chemistry. This scenario could be mistaken for mineral dissolution.

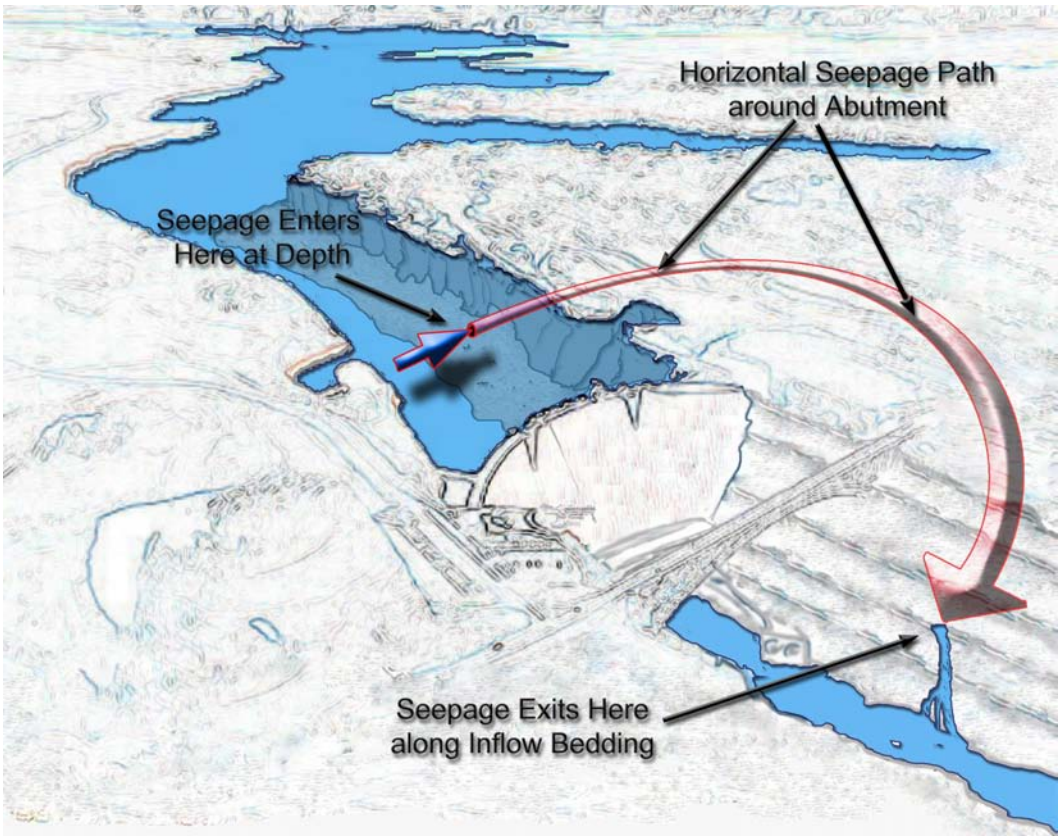

Figure 2c.—Diagram showing time-lagged and horizontal flow of higher concentration reservoir water at depth around the abutment of a dam. This scenario could be mistaken for mineral dissolution.

An important conclusion from the Glen Canyon Dam study is that seeps closer to the dam are more important for seepage chemistry assessments because (1) they are closer to the embankment and have greater potential structural implications; and (2) they are likely more direct flow paths lacking the ambiguities associated with delayed flows and higher reservoir concentrations at depth.

Summary of Other Processes Affecting Seepage Chemistry

Several other processes besides mineral dissolution may also change the chemistry of seepage and should be considered along with mineral dissolution. These processes may include bacterial respiration and metabolism; cation and anion exchange; mixing of reservoir water with a near-surface native aquifer; and delayed horizontal flow of deep, higher-concentration reservoir water through foundation and abutments. Each of these processes can change seepage chemistry, both to increase and/or decrease concentrations during seepage transit. The important point is that not all increases in seepage chemical concentrations are caused by dissolution processes; nor do increases automatically suggest structural impairment. Conversely, engineers should be HIGHLY concerned if new seepage is appearing near a dam that is very similar to reservoir water, as this suggests a potentially dangerous direct flow path. The author recommends Atlas and Bartha's *Microbial Ecology—Fundamentals and Applications* (1998), for more information on biotic processes. Freeze and Cherry's *Groundwater* (1979) and Domenico and Schwartz's *Physical and Chemical Hydrology* (1990) are often cited for background on groundwater movement and transformation. Cedergren's *Seepage, Drainage, and Flow Nets* (1989) is a practical reference for engineers.

A Note about Unchanging Concentrations

Just as we should not assume that increases in seepage concentrations mean dissolved mineral void formation in a structure, it is very important to note that seepage showing no change in concentration from reservoir water may not be good news. This situation indicates that reservoir water is flowing fairly quickly and directly to the seepage emergence point. If seepage flows and emergence zones are increasing with no concentration increases, this is a definite structural danger sign!

Mineral Dissolution and Dam Seepage

Because of the hydraulic heads associated with reservoirs and the heterogeneity and imperfections in structural geology, all dams leak and have seepage (Cedergren, 1989). Not all seepage warrants concern, but all seepage flows should be monitored for changes by field personnel familiar with a given dam. This section examines how seepage might develop in and around a dam, and how chemical concentrations change over time in seepage.

Seepage in a New Structure

After initial reservoir filling, water begins to flow around the abutments and through the foundation. In the case of earthfill dams, water also begins to flow though the embankment. If the geology is fairly uniform and unfractured, seepage flows behave much like groundwater, with flow rates, the phreatic surface, and seepage residence times dependent on the permeability of the structural formations and the hydraulic head imposed by the reservoir. If initial seepage flows encounter soluble minerals, the most soluble dissolve and create a solutioning front of higher concentration ions. When this “first flush” of seepage emerges, it will likely contain a higher concentration peak that will diminish as the readily available minerals are dissolved and then depleted along flow paths (Muckenthaler, 1988; Cedergren, 1989). Much higher seepage concentrations compared to recent samples were observed at Horsetooth Dam in the 1951 postfilling SM-3 samples, that emerged from a limestone karst outcrop 3,000 feet downstream of the dam (Craft, 1999). Initial filling at Horsetooth Dam produced a new reservoir-dominated aquifer that contacted previously undissolved geologic strata and mobilized readily available soluble minerals. Figure 3a shows a graph of the theoretical seepage concentration gradient expected on first filling, or when a new seepage flow path opens up.

Seepage in Formations with Minimal Soluble Minerals

In the real world, structural geology is not uniform—even in massive sandstones such as those at Glen Canyon Dam. Seepage flow follows the path of least resistance along cracks, fissures, faults, and seams between strata. As seepage flows over time, calcite and amorphous silica present in trace to minor amounts as cementing agents dissolve and increase the permeability of the structural rock in sandstones, porous volcanic rock, and other nonlimestone sedimentary rocks. Figure 3b shows a closeup view of how seeps may form over long time periods in a sandstone or siltstone. Note that the seepage voids shown in blue are exaggerated for illustration purposes. Often, these seeps can become steady state

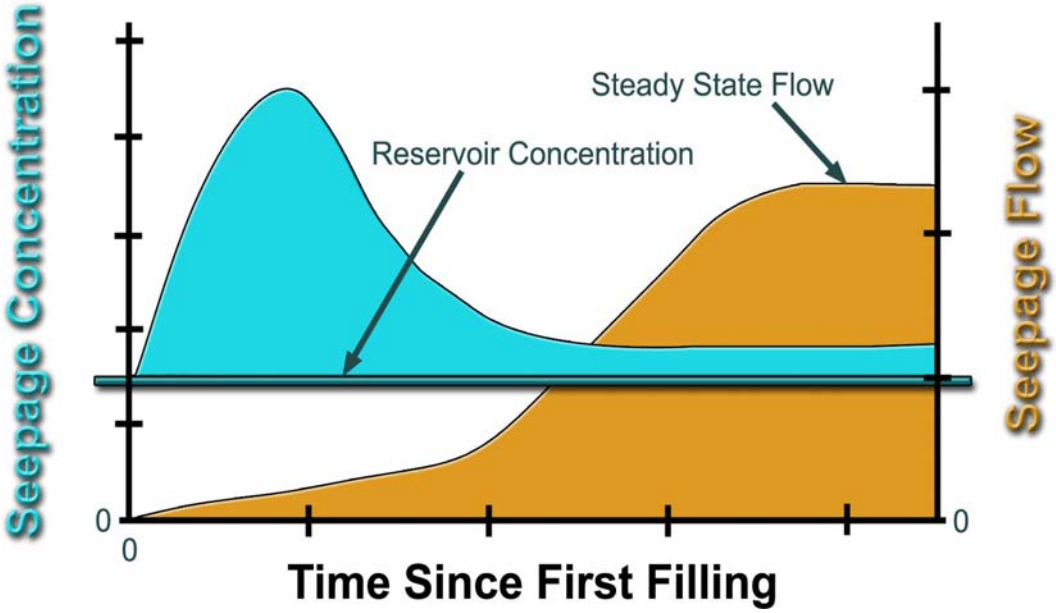

Figure 3a.—Plot of theoretical solutioning front transient concentration increase (blue) expected on first filling of a reservoir. This two-variable plot also shows how seepage flow (orange) would be expected to increase and then reach a stable, steady state flow condition.

flows that do not increase, or progress, over time with the same reservoir elevations.

Seepage in Karst and Massive Soluble Formations

The biggest concern to engineers is the presence of massive limestone, gypsum, and anhydrite deposits in close proximity to the dam, especially when they occur in karst terrains. These common terrains contain significant fracturing and voids (often previously formed by acidity from bacterial activity in groundwater) that create enhanced seepage flow paths that have led to structural slumping, piping, and dam failures (Muckenthaler, 1988; Maksimovich and Sergeev, 1983). In many karst systems, the groundwater flow cannot be characterized as a typical aquifer, but rather as a network of underground streams. Karstic strata also often contain unconsolidated layers and breccias that provide high-permeability zones adjacent to soluble mineral deposits where increased seepage flows can lead to structural problems (James and Lupton, 1978; James, 1985; Jacobs et al., 1988).

The progression of void formation in karst has been studied extensively for many years (Davies, 1960; Thrailkill, 1968; Vandike, 1985; James, 1981), and fundamentally, void paths are likely to enlarge over time if seepage is undersaturated with respect to the soluble mineral along a flow path. As void paths enlarge, enhanced flows accelerate mineral dissolution through turbulent mixing. At some point in this progression, higher flows introduce shear forces

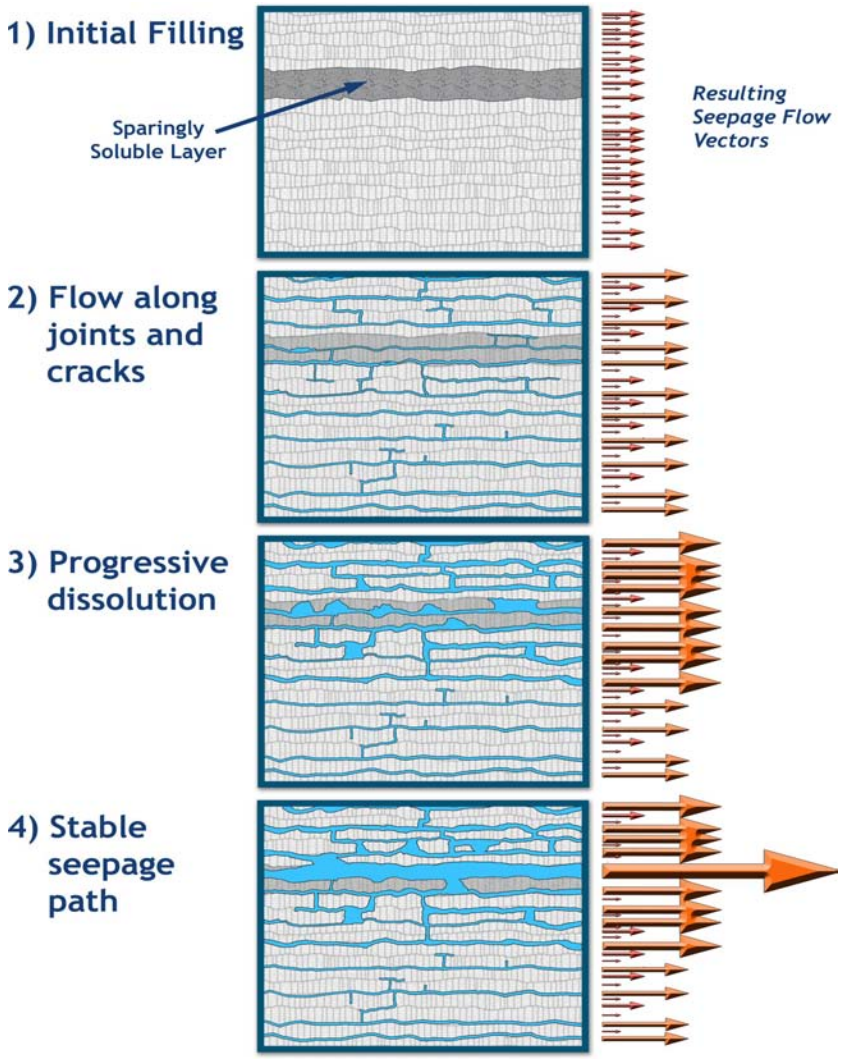

Figure 3b.—Possible seepage progression in a sandstone or siltstone formation having calcite or amorphous silica as cementing agents, but no significant deposits of soluble minerals. These cross sections show layers and small fractures, and seepage flow is from left to right. Void spaces are exaggerated for illustration purposes. The arrows to the right of the cross sections are flow vectors, with greater flow implied by larger arrows. This process could account for gradual increases in permeability or the formation of small, stable seeps developing over decades.

adequate to erode materials and lead to piping and structural failure (Dreyboldt, 1987; James and Kirkpatrick, 1980).

Figure 3c provides a hypothetical example of progressive development of seepage for a dam sited over soluble mineral deposits in a karst environment. Note the bottom panel, where sinkhole collapse has produced a direct hydraulic path between the reservoir and seepage effluents. Once again, seepage flow paths in blue are exaggerated for illustration.

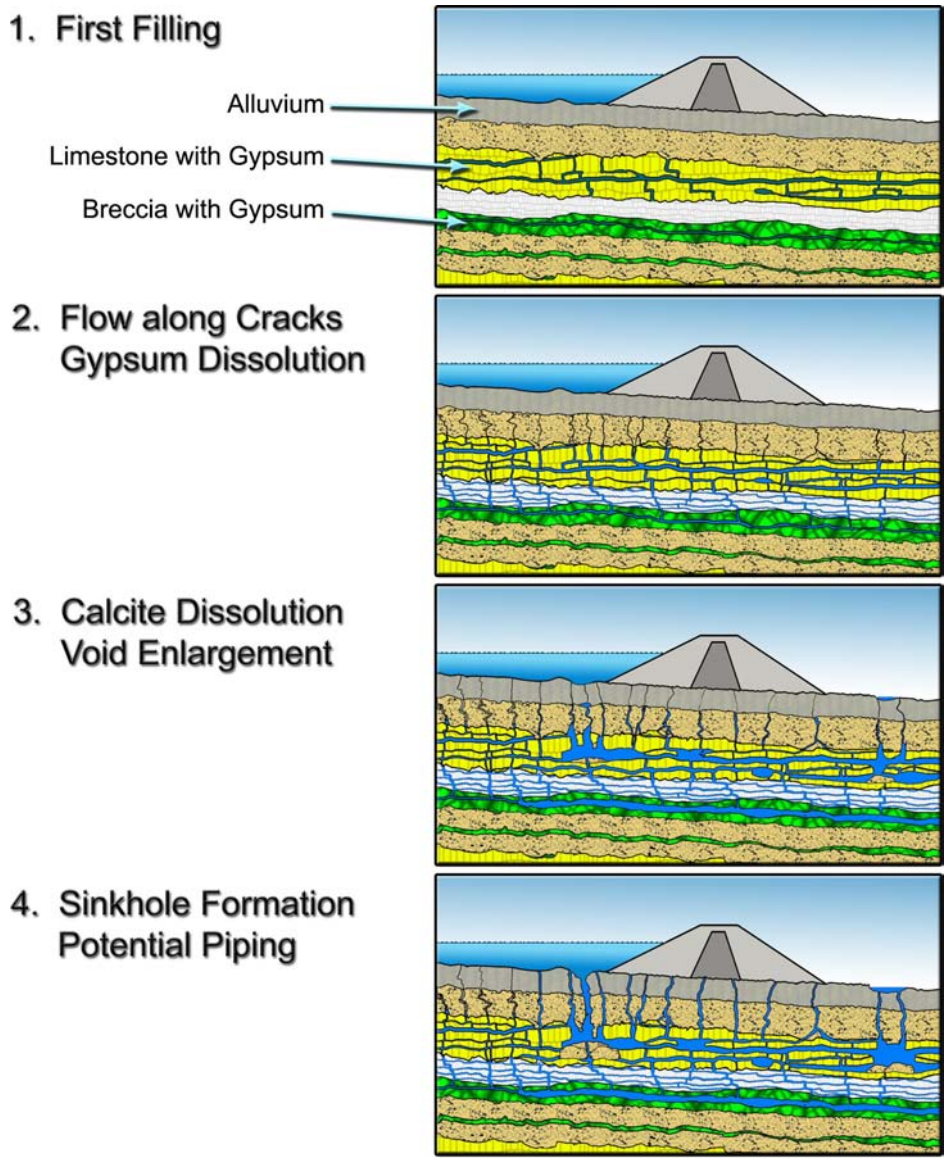

Figure 3c.—A possible scenario for development of seepage problems at a dam sited on fractured karst terrain. Cross sections of a dam are shown as seepage progresses and worsens from top to bottom. Void spaces are exaggerated for illustration purposes.

When and Where Should Seepage Samples Be Collected?

Any dam or embankment showing changes in seepage patterns over time, that is sited on limestones, breccias, and other porous sedimentary rocks with evidence of gypsum, anhydrite, calcite, dolomite, or soluble evaporite deposits should be considered a potential seepage monitoring site. The closer these formations are to the dam, the greater is the potential structural risk from mineral dissolution. The Reclamation Dam Safety Office has established the Comprehensive Facility Review (CFR) process, which applies a standard methodology to identify existing

dams that might be at structural risk. The CFR report sometimes recommends that seepage sampling be evaluated for a structure thought to be at risk from mineral dissolution.

Importance of Baseline Data Sets

Baseline data sets are important for comparing later seepage data. Seepage sample collection and analysis is recommended after seepage has stabilized after initial reservoir filling or after repairs and modifications to a dam. Samples for baseline or postconstruction seepage chemistry programs should be collected 1 to 2 weeks after minimum and maximum reservoir elevations. Minimum or low-water samples, usually occurring in fall after the irrigation season, provide an indication of deeper and slower seepage flows with longer foundation or abutment residence times, and an opportunity to evaluate the effect of longer residence time on seepage chemistry. Maximum or high-water samples, usually collected in late spring or early summer after snowmelt runoff has filled the reservoir, provide information on seepage when hydraulic head is greatest. Higher sampling frequency might be warranted in some structures, but the minimum seepage chemistry sample collection level should include low and high water levels.

Physical Site Inspection

After baseline or postrepair data sets are established, the primary criterion for collecting seepage samples should be based on observation of changes in seepage behavior. The most important clues should come from physical inspection by project personnel who have intimate familiarity with the dam's physical structure and seepage over many hydrologic cycles. Experience counts! Important seepage issues to note include observation of new seeps, spreading of a seepage outflow, increased or unusual flows, and development of cloudy flows containing suspended particles. Important structural changes to note include slumping, cracking, progressive changes in structural features, guard rails, and road signs. These are the direct indicators that alert project managers to potential seepage problems and the need for seepage sample collection and closer flow and piezometer well monitoring.

Figure 4a shows how a seepage emergence wet spot appears on a downstream abutment below a dam built on karst terrain. A wet spot can be observed along downstream abutment features by the bright green or dark green contrast compared to the surrounding surface, and greater vegetation growth. If wet spots like this, photographed below Carter Lake Dam, Loveland, Colorado, increase in size over several seasons with similar runoff and reservoir fluctuations, it may suggest that seepage along this flow path is progressing and warrant closer scrutiny. Figure 4b shows a small v-notch weir installed below a flowing surface seep photographed below Carter Lake Dam.

Flow and Phreatic Surface vs. Reservoir Elevation

Beyond direct observation of changes at the site, the next most important criterion is the ongoing evaluation of consistently measured seepage flows and piezometer levels. These are the *most important* data providing the best indication of a

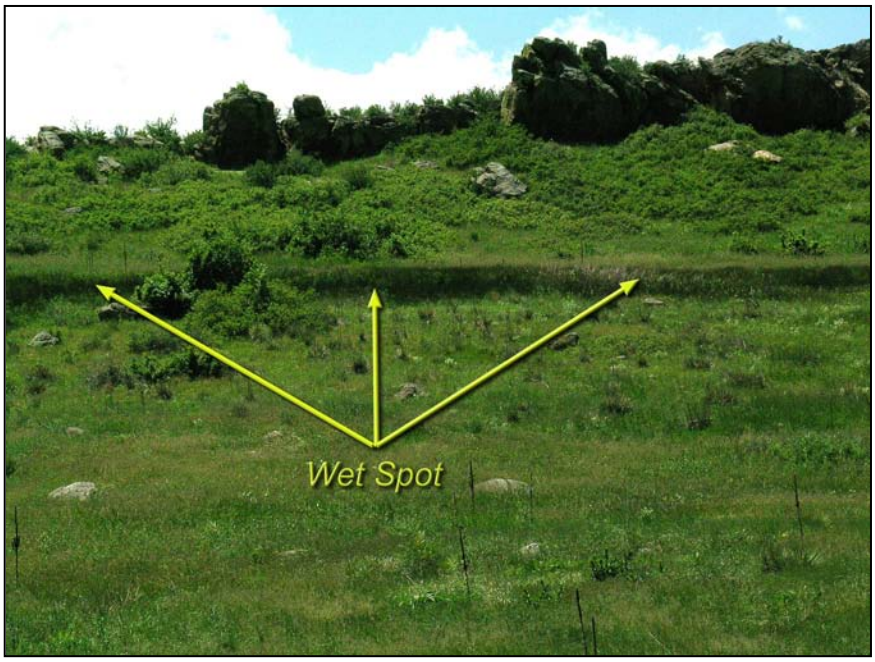

Figure 4a.—Seepage emerging along an downstream abutment as a wet spot. Increases in the areal extent of such wet spots over several hydrologic cycles suggest seepage progression. This photo shows the right abutment downstream of Carter Lake Dam, Loveland, Colorado.

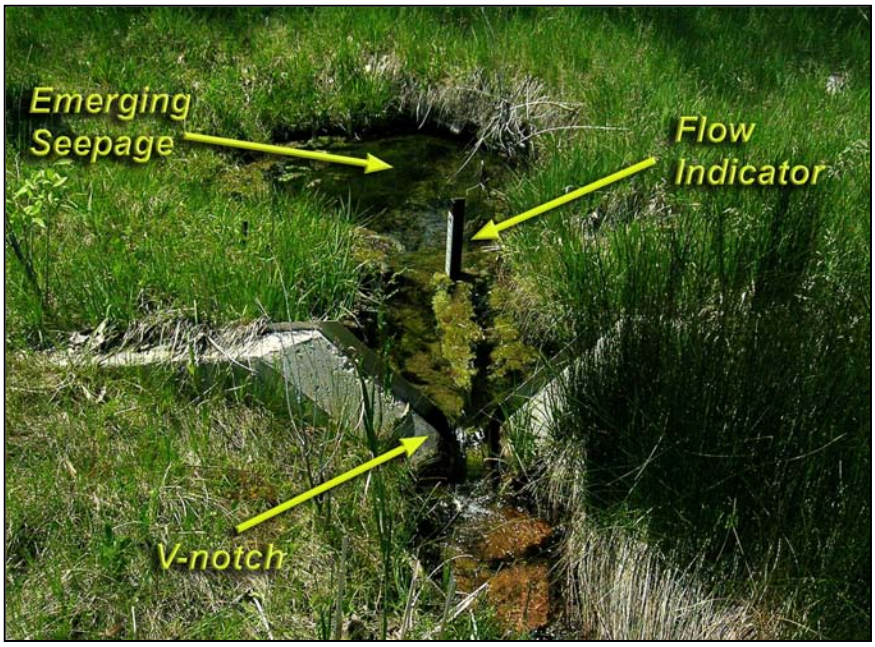

Figure 4b.—Seepage emerging as a surface flow behind a V-notch weir at Carter Lake Dam, Loveland, Colorado. Seepage flow can be measured and compared to reservoir surface elevations to determine whether seepage is stable or progressing.

potentially dangerous situation when seepage samples should be collected and analyzed. If seepage is stable and steady state, then the same flows and piezometer levels should be seen for the same reservoir elevation, and the chemistry data are also similar. When seepage flow increases for the same historical reservoir elevations, then seepage is progressing (increasing) and flow paths are widening.

When to Collect Seepage Samples

Seepage samples should be collected and analyzed under the following circumstances:

- When a dam is sited on geology susceptible to mineral dissolution and has developed seepage problems, or when the Dam Safety CFR recommends seepage testing

- After first filling or postrepair at a dam when normal seepage patterns have been established. Seepage samples should be collected and analyzed at maximum and minimum reservoir elevations for several years to establish a baseline data set.

- Whenever physical site inspection reveals unexpected changes in seepage or structural behavior

- Whenever flows and piezometer levels are increasing for previous identical reservoir elevations

Where to Collect Seepage Samples

Always measure field pH and temperature (T) for seepage and reservoir samples *in situ* using calibrated portable meters. Appendix 1 provides example sample submittal forms for seepage samples and sources for field equipment and services. Use the following general rules to choose collection stations:

- Collect reservoir water behind the dam and at depth using a Van Dorn or Kimmerer sampler (see procedures section below) during summer and winter when reservoirs are likely to be stratified. Surface grab samples are fine during spring and fall after reservoir overturn. Summer and winter samples, however, should include a depth profile of the reservoir for pH, T, EC, DO, turbidity, and redox potential using a multiprobe.

- Collect surface seepage as close as possible to the dam. As you move farther downstream, the likelihood is greater that the sample is of mixed origin, or seepage flow paths are not close to abutments or foundation. While downstream springs and seeps might be sampled when seepage chemistry programs begin for baseline information, their routine collection may not be necessary.

- Collect samples from established seeps at the weir, and only when flow is measurable. If water is seeping but it is below the weir, then a sample should be collected as close as possible to its emergence point. Make an attempt to estimate or measure seepage volume.

- Collect samples from new seeps and sand boils at the emergence point.

- Collect well and piezometer samples only from tubes and wells that intersect the geology of concern. Collect samples only from active piezometers that are being currently read. Independently measure depth to water surface before sampling piezometers and wells.

- Always collect samples from wells that become artesian.

Interpreting Seepage Chemistry and Mineral Dissolution

This section addresses some basic concepts about how to interpret chemistry data from reservoir, seeps, and wells at a dam where seepage is a concern. This process is not simple and dam safety engineers are advised to seek help from experienced geologists, geochemists, and analytical chemists. The general approach for interpreting seepage chemistry data is:

- Plotting the available data on Stiff, Piper, or radar diagrams, and grouping related plots (for example, all wells intercepting a particular formation) with the reservoir polygon for visual comparison.

- Calculating *mineral saturation indices* (SI's) for each sample using a computer chemical equilibrium program such as WATEQ4F (Truesdale and Jones, 1973; Ball, et al., 1987), MINTEQA2 (Allison et al., 1991), or PHREEQE (Parkhurst, et al., 1980), and examining differences between reservoir and seepage.

- Calculating difference data between seeps and reservoir concentrations. These data are converted from mg/L to millimoles per liter (mMol/L) or meq/L concentrations and then graphed on difference plots.

- Determining the effect of mixing on the observed concentration differences by applying mixing models, such as NETPATH (Plummer, et al., 1991) or stable isotope investigations (Epstein and Mayeda, 1953).

- Development of a geochemical mass balance model to help account for difference data not attributable to mixing.

- Results of the mass balance model are used to identify the fraction of the increase in seepage concentrations that is caused by specific mineral dissolution reactions. These data are then used to calculate flow-weighted mass wasting and void formation associated with particular soluble minerals.

Graphical Data Presentation

Chemical data can tell a clear story about seepage transformations when plotted on comparative graphs such as Stiff diagrams, Piper diagrams, radar diagrams (fig. 1), difference diagrams, and other multivariate plotting techniques. Plotting the data should be considered the first step in any seepage chemistry interpretation process, and good plots also provide clear visual support for conclusions derived from other interpretative methods.

Polygon Plots

One of the best ways to use polygon plots is to group seepage and well plots with reservoir water plots, as seen in figure 5a, which shows Stiff diagrams plotted for seepage and reservoir data from Horsetooth Dam, Colorado-Big Thompson Project, Ft. Collins, Colorado. Figure 5a compares seepage data from one year to the next and includes the reservoir chemistry as the smaller blue-green polygons on each seepage Stiff diagram. These Stiff diagrams were created using the AquaChem program (Waterloo Hydrogeologic, Inc., version 4) and were combined for presentation using the Photoshop® CS program (Adobe, Inc, version 8.0). Figure 5b shows Stiff diagrams plotted on a plan elevation map of a dam. Geologic cross-sectional drawings can also be similarly annotated. This approach is a good method to associate chemistry with specific structural features or geological strata, and public domain software is available to plot Stiff diagrams on geographic information system maps (Boghici and Boghici, 2001).

Classification Plots

Classification plots are multivariate graphs that can be used to classify samples based on similarities in a set of variables. Multivariate statistical techniques like principal components analysis, discriminant analysis, or cluster analysis can also produce classification plots using multiple variables. Classification is based on clustering of samples in the plotting space. A good example of a simple classification plot is the the Piper diagram (Piper, 1944), seen in figure 5c.

Piper diagrams have been used for may years as a simple graphical method for visualizing seepage and reservoir chemistry and to classify seepage waters according to their dominant cations and anions. This classification is often called the water type, and is used by geochemists to group and characterize groundwaters having similar geological origins, aquifers, or flow paths. Water types are usually denoted by their dominant cations and anions. For example, a Ca-HCO3 or Ca-Mg-HCO3 water would be expected for a groundwater aquifer located in limestone. A Ca-SO4 water type would be expected in a groundwater exposed to gypsum or anhydrite.

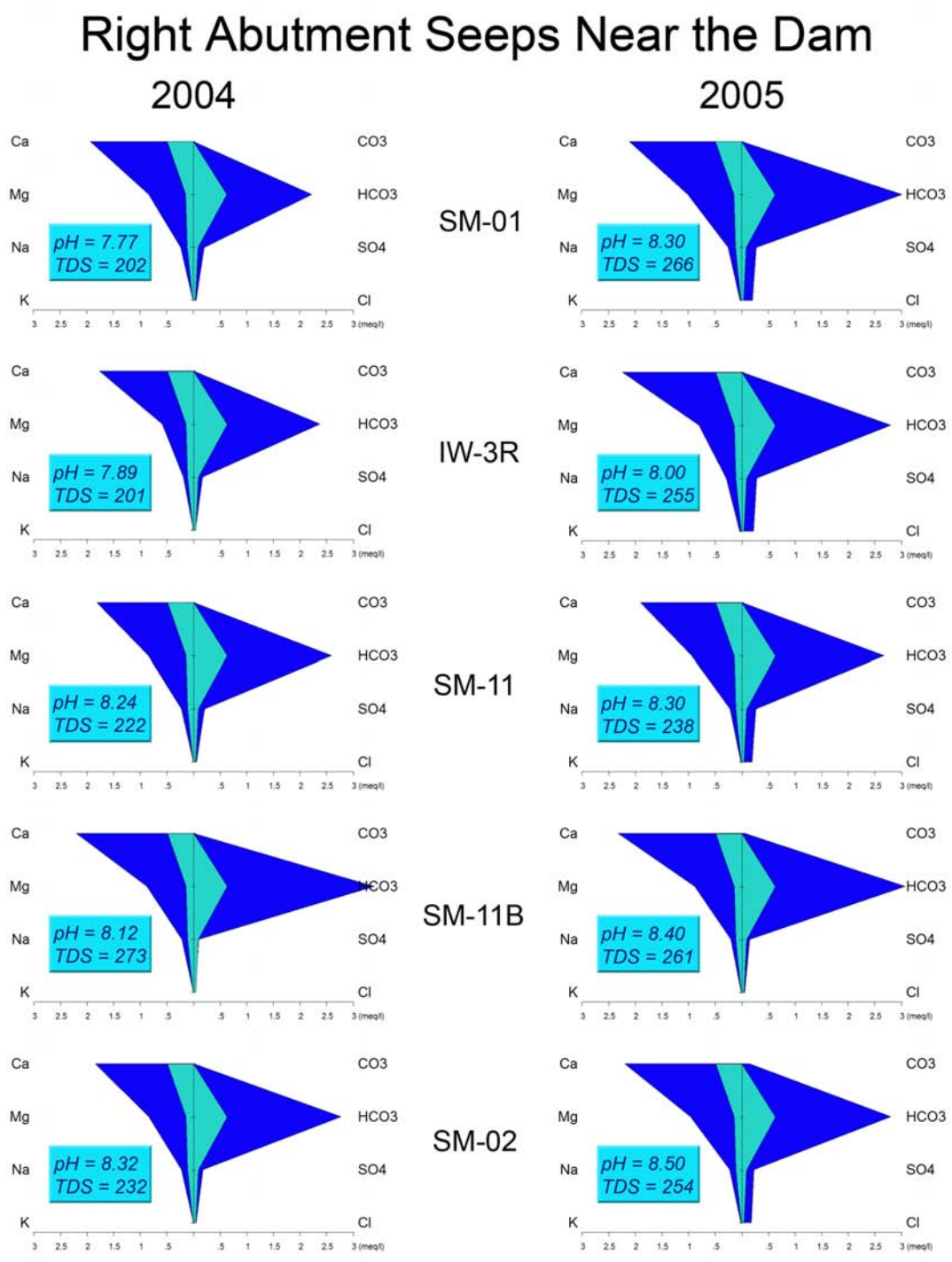

Figure 5a.—Comparison of seepage and reservoir chemistry data using Stiff diagrams, plotted using the AquaChem program. Reservoir chemistry is included on each seepage diagram as the smaller light blue green diagrams. See appendix 1 for plotting software sources.

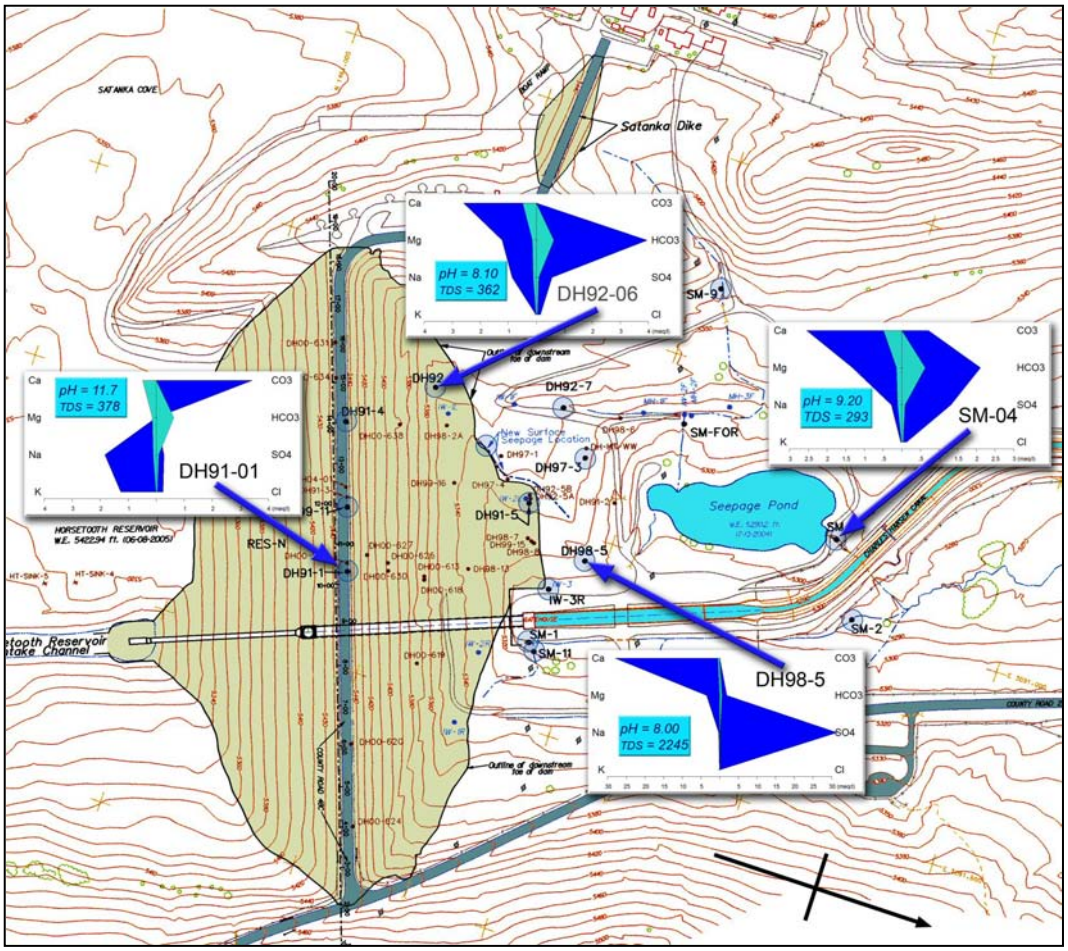

Figure 5b.—Stiff diagrams showing seepage and reservoir chemistry plotted on a plan map.

The Piper diagram is composed of two bottom ternary diagrams, with each ternary diagram having an axis along each of the triangles, and a central parallelogram. Altogether, these three plotting spaces form a larger triangle. The ternary plots use mole percent data for cation and anions. The left bottom triangle plots cation data, and the right bottom triangle plots anion data. Lines from the plotted points for a seepage water in the cation and anion ternary diagrams are then extended parallel to the sides of the larger triangle and intersect in the parallelogram. These points define the geochemical "type" of the water. Similar origin waters cluster together in the parallogram coordinate space, and most Piper diagram programs allow a scaling of plotted symbols to reflect TDS or other water quality variables. Figure 5c shows several seepage samples from Horsetooth Dam that fall into different geochemical water types.

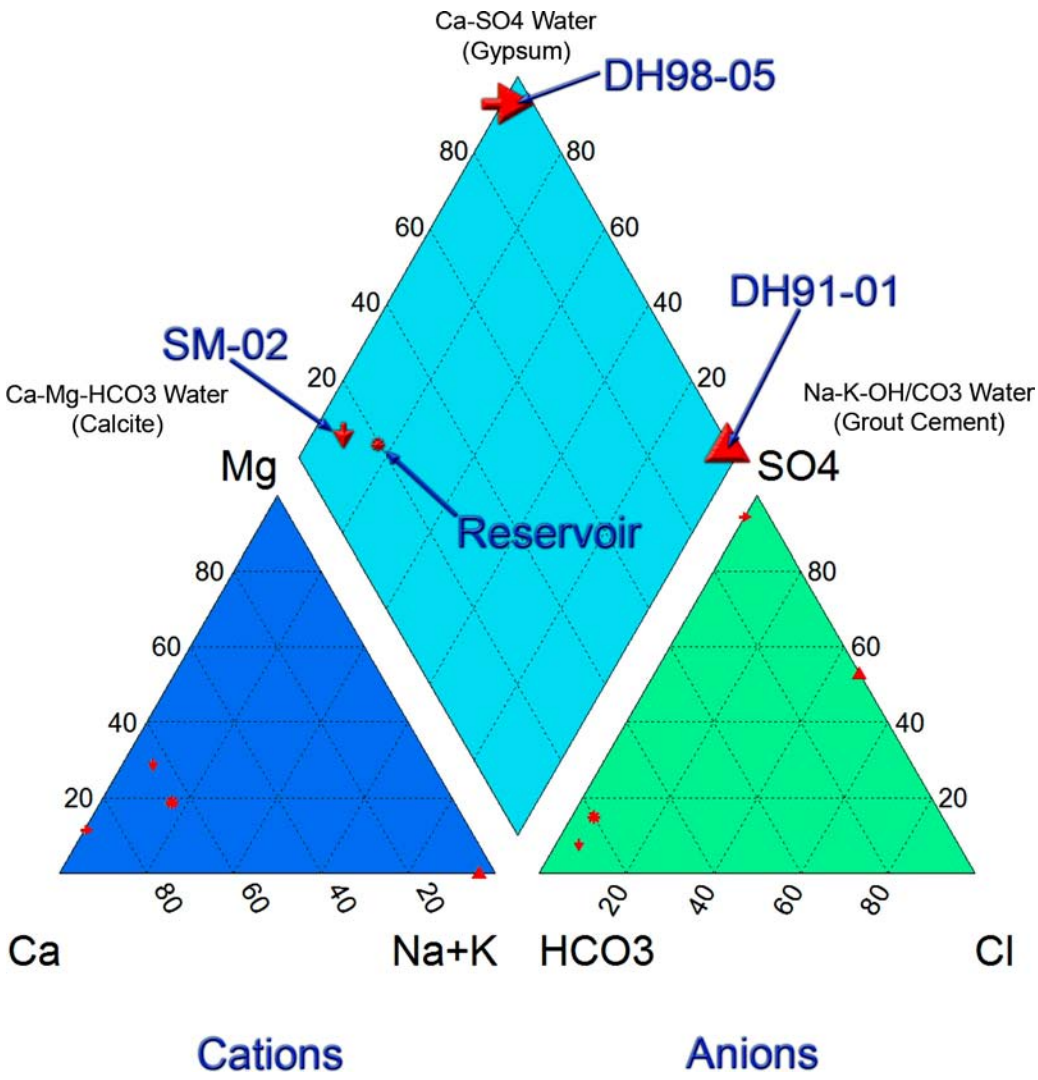

Figure 5c.—A Piper diagram that plots major ions data for seepage as mole percentages on ternary diagrams for cations (blue) and anions (green). The ternary diagram points are then projected into the parallelogram (blue-green) where similar geochemical water types will cluster together. The waters are named based on their dominant cations and anions. The relative sizes of the plotting icons are scaled to represent the TDS of the seepage water.

Mineral Saturation Index Calculations Using Computer Models

Computer chemical equilibrium programs such as MINTEQA2 (Allison et al., 1991), and PHREEQE (Parkhurst, et al., 1980) are part of the essential toolbox for geochemical interpretation of seepage chemistry data. These models treat chemical reactions as algebraic equations and mathematically “equilibrate” the water chemistry using numerical methods based on the concentrations entered into the model and a data base of possible chemical reactions and equilibrium constants expected to occur in water. These models also calculate a mineral

saturation index (SI) for common soluble minerals, one of the most useful output parameters for seepage evaluations. The SI is denoted as "Log AP/KT" in both the MINTEQA2 and PHREEQE models' output tables. Appendix 2 provides a standard operating procedure for entering data and running an MS-DOS version of the MINTEQA2 model and the data entry program, PRODEFA2. Versions that run in the Windows operating system are commercially available (see app. 1).

How MINTEQA2 Works

MINTEQA2 evaluates chemical concentration data and calculates SIs for minerals potentially responsible for the particular sample's chemical concentrations. Mathematically, the SI represents the base-10 logarithm of the *activity product* (AP) divided by the product of the *equilibrium constant* (K) and the *temperature* (T) in degrees Kelvin. The calculation refers to a specific reaction, such as calcite dissolution:

$$CaCO_3 + H^+ \text{ =4444< } Ca^{2+} + HCO_3^- \qquad \text{Eq. 17}$$

with an equilibrium constant, *K*, defined at T = 25 °C (298.15 °Kelvin) as:

$$K = \frac{[Ca^{2+}]*[HCO_3^-]}{[CaCO_3]*[H^+]} = 4.79\times10^{-9}$$

The chemical species noted within [brackets] represent the *activity* (in moles per liter) for that particular component in the given reaction. Activity is the thermodynamic version of concentration at chemical equilibrium, and it is calculated by multiplying measured concentration times the *activity coefficient* for the given component. At low total ionic strength, the activity coefficient approaches 1 and there is no significant difference between concentration and activity. As total ionic strength increases, however, the activity coefficient acts to reduce the measured concentration of a particular ion for thermodynamic calculations. The activity product, *AP*, is determined by multiplying the calculated activities for the expected *products* of the calcite dissolution reaction, Ca^{2+} and HCO_3^-. Basically, the SI is a comparison of measured concentrations in water (adjusted to represent activity) to concentrations that would be expected if calcite and water were at equilibrium.

So, a positive value for the calcite log(AP/KT) suggests that reaction products are greater than expected at equilibrium, and thus the water is oversaturated with respect to calcite. This means that calcite will tend to *precipitate* out of solution. A value of log(AP/KT) = 0 (in other words, (AP/KT) = 1) indicates that the water is at equilibrium with calcite. Negative values suggest that the reaction products are lower than expected at equilibrium, and the water is undersaturated with respect to calcite. These waters will tend to *dissolve* calcite. To summarize:

Negative log(AP/KT) means undersaturated: ***potential dissolution***
Positive log(AP/KT) means oversaturated: ***potential precipitation***

Increasing (less negative) SI between reservoir and seepage samples suggests possible mineral dissolution, or mixing with a higher concentration water along the flow path. **Decreasing** (more negative) SI between reservoir and seepage samples suggests possible mineral precipitation, or dilution mixing with a lower concentration source of water.

The MINTEQA2 model also calculates the mass distributions of all possible aqueous chemical *species* based on the *components* entered into the model. Components are the MINTEQA2 "master input variables" that correspond to the measured chemical concentrations, and each component is linked to a set of secondary reactions that are used to calculate all the various species associated with a set of components in water. For example, entering sulfate, MINTEQA2 SO4-2, component number 732, and calcium, component Ca+2, number 150, results in equilibrium estimates for the aqueous free ions of calcium and sulfate (SO_4^{2-} and Ca^{2+}), but also the dissolved aqueous ion pair, CaSO4 AQ, species number 1507320. The amount of CaSO4 AQ formed depends on the input component concentrations, the data base value for the equilibrium formation constant, *K*, and the stoichiometry (the coefficients for the relative molar amounts of the components that form 1 mole of product) of the assumed chemical reaction. MINTEQA2 includes a data base with equilibrium constants, *K*, and stoichiometry for most of the reactions expected to occur for an entered set of components. Partial pressures of various gases, such as O_2 and CO_2 may also be entered and their reactions with components solved for the set of input concentrations.

MINTEQA2 Assumptions and Limitations

While the MINTEQA2 model calculates a wealth of output, several important assumptions are required for accurate output estimates:

- Like all complex computer models, the saying "garbage in, garbage out" applies in force. The input data need to be accurate and comprehensive for the problem to be modeled accurately. Problem data sets need to include both major anions and cations, and the data need to be accurate and precise. The cations and anions should also be equal in meq/L concentration.

- Conditions such as temperature, pH, dissolved oxygen, redox potential, and partial pressures of atmospheric gases should match the sample field conditions. Lab pH and redox (Eh) measurements are often different than those found in *in situ* groundwaters, which are often under pressure and experiencing anaerobic or reducing conditions (Morel and Hering, 1993). Such a groundwater begins to change immediately upon exposure to surface atmosphere, and the changed sample is what the lab analyzes. On the other hand, MINTEQA2 can also simulate *what if* scenarios where the input water is equilibrated with solid phases, and pH and Eh are set to fixed values.

- The primary thermodynamic assumption is that the water that MINTEQA2 is modeling is at chemical equilibrium, with no net flux of concentrations, or

energy. In natural surface waters containing biological activity, this assumption is seldom met since these systems are constantly exchanging energy with the external environment. Natural waters are in a "steady state"—a type of dynamic equilibrium with the surrounding environment, but this is not the same as thermodynamic equilibrium.

- The equilibrium assumption ignores the rates of data base reactions (Brezonik, 1994). MINTEQA2 is called a "geochemical assessment model" and was developed primarily as an application for groundwater systems. Natural groundwaters that flow very slowly through a homogeneous-geology aquifer may meet equilibrium assumption requirements; however, seepage at a dam may flow quickly through permeable paths, and limited contact time with geologic materials may not allow slow reactions to go to completion. The simulation by MINTEQA2 is also limited by the thermodynamic data base, which contains equilibrium constants from a variety of sources and experiments (Garrels and Christ, 1965; Hegelson, 1969; Van Zeggeren and Storey, 1970).

- The final *caveat* regarding interpretation of MINTEQA2 data, is that not all possible reactions are included in the model's thermodynamic data base. For example, almost all the reactions in the MINTEQA2 thermodynamic data base represent *congruent* dissolution reactions, such as complete dissolution of calcite to form constituent ions. Secondary, or *incongruent* weathering reactions, such as the conversion of kaolin to smectite, are not included (though the thermodynamic data base can be augmented by experienced users). If the system under study happens to depend on secondary or incongruent reactions for the water chemistry concentrations, MINTEQA2 estimates suffer accordingly.

Difference Data

Difference data (denoted as $_i$, where i represents the measured ion), are easily calculated by subtracting reservoir water concentrations from seepage water concentrations, and provide a general indication of what might be causing the increases in seepage concentrations. Difference data provide valuable information about changes in constituent concentrations that occur as the reservoir water moves through the foundation and finally emerges as seepage. Positive difference values indicate a net gain during seepage transit for a given constituent that could be caused by dissolution, mixing, delayed flow, or bacterial processes. Negative values suggest a net loss for a given constituent that could be due to precipitation, bacterial respiration, or cation exchange. Figure 6 shows a difference plot that allows visualization of the changes occurring between reservoir and seepage. In this example, there is an indication of a small amount of ion exchange that has caused an increase in Na, and some congruent dissolution of calcite that also contains some Mg. However, before we can calculate mass

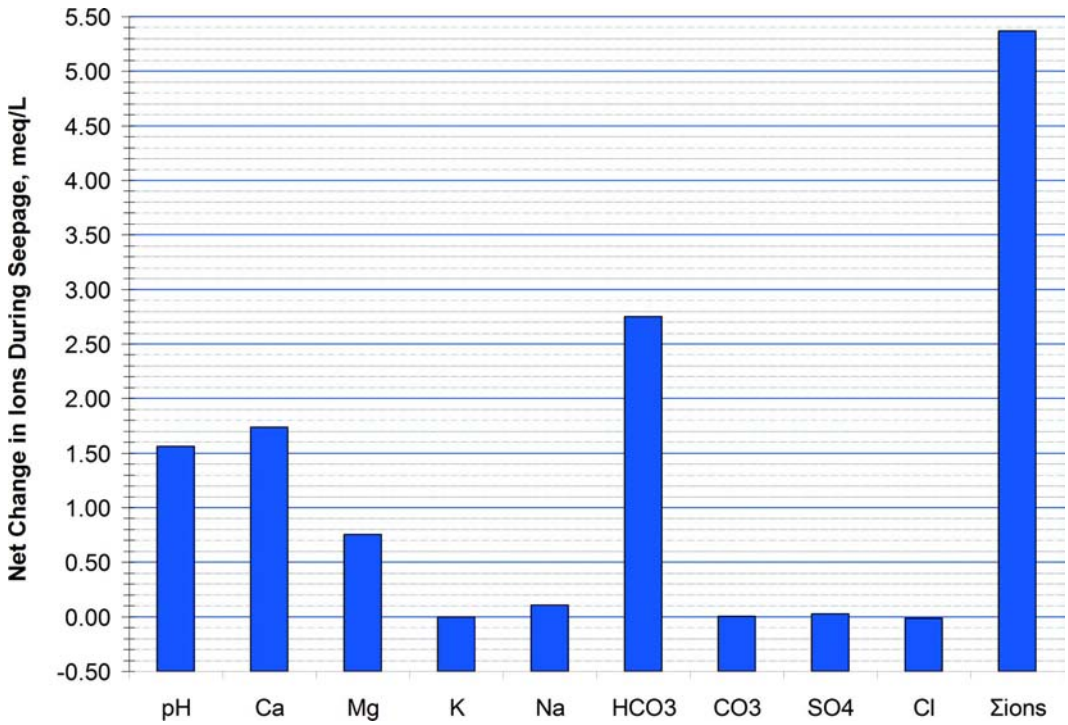

Figure 6.—A difference plot showing the changes between reservoir and seepage chemistry concentrations. The increase in pH and lack of change in SO_4^{2-} does not suggest significant biotic activity, and increased Na suggests some possible ion exchange. These data suggest simple congruent dissolution of calcite that also contains some Mg.

wasting and void formation associated with mineral dissolution, we need to develop what is called a *mass balance model*.

Mass Balance Models

Mass balance models are a tool used by geochemists to account for changes in water quality caused by weathering and mineral dissolution. The input data we need to develop a mass balance model are the concentration changes between a source water (the reservoir water) and the resulting groundwater (the seepage water). The difference data provide the clues suggesting that certain chemical processes are occurring during seepage transit. Table 4 provides a summary of the processes that may account for changes in seepage concentrations.

Mass balance models are a proposed set of processes and chemical reactions thought to produce the changes observed in seepage chemistry that are consistent with available geological evidence. While a good mass balance model can be semiquantitative in accounting for changes in seepage chemistry, development and application are not simple. The general approach suggested by Garrels and MacKenzie (1967), Drever (1988), and others (Plummer and Back, 1980;

Table 4.—A summary of potential causes for increases and decreases in seepage concentrations that are common in dams

Constituent	Seepage concentration increase	Seepage concentration decrease
pH	• calcite dissolution • contact with grout if present and pH > 9	• aerobic and anaerobic biotic activity if DO or OC also decreases
Ca^{2+}	• calcite or dolomite dissolution • gypsum or anhydrite dissolution if SO_4^{2-} also increases • ion exchange if Na^+ decreases	• ion exchange if Na^+ also increases and clays present
Mg^{2+}	• calcite or dolomite dissolution • congruent dissolution of magnesium silicates (chlorites, pyroxenes, amphibole) if present • mixing with higher concentration groundwater	• incongruent dissolution • dilution with lower concentration groundwater
Na^+	• ion exchange • halite dissolution if Cl also increases • mixing with higher concentration groundwater • contact with grout	• ion exchange if Ca^{2+} increases and clays present • dilution with lower concentration groundwater
K^+	• ion exchange • incongruent dissolution of K-feldspars to kaolinite • contact with grout	• ion exchange
CO_3^{2-} - HCO_3^- - OH^-	• congruent dissolution of carbonate minerals • aerobic and anaerobic biotic processes • contact with grout - OH^-	• not likely—methanogenesis only • dilution with lower concentration groundwater
Cl^-	• halite dissolution • mixing with higher concentration groundwater	• dilution with lower concentration groundwater
SO_4^{2-}	• gypsum or anhydrite dissolution	• anaerobic biotic activity, especially if H_2S odor present • dilution with lower concentration groundwater
SiO_2 or H_4SiO_4	• congruent dissolution amorphous silica (glass) • congruent dissolution of silicate minerals • incongruent dissolution	• incongruent dissolution • dilution with lower concentration groundwater
Fe and Mn	• anaerobic biotic activity	• adsorption on particulates
Al	• congruent and incongruent dissolution of aluminosilicates • contact with grout	• adsorption or precipitation
OC	• not likely	• aerobic and anaerobic biotic activity
N and P	• aerobic and anaerobic biotic processes	• not likely • dilution with lower concentration groundwater
DO	• not likely	• aerobic biotic activity

Jacobs, et al., 1988) is recommended and should be applied by someone with geochemistry experience.

Balanced Chemical Reactions

The mass balance approach involves developing balanced chemical equations for all the major reactions and processes thought to occur at a given dam. These reactions could include bacterially mediated processes (DO and OC depletion, sulfate reduction, and aerobic and anaerobic respiration/metabolism, partial or incongruent weathering of one mineral to another and releasing and/or consuming ions in the process, congruent or complete dissolution of minerals, and cation exchange (Drever, 1988; Atlas and Bartha, 1998; Stumm and Morgan, 1996; Hem, 1992; Morel and Hering, 1993; Deer, et al., 1992). Mixing or dilution can also be included as a component process in a mass balance model, and computer models like NETPATH (Plummer, et al., 1991) may be used to evaluate whether chemical changes between reservoir and seepage may be caused by mixing of reservoir water with another groundwater—perhaps a preimpoundment aquifer. These results can be used to rule out mineral dissolution reactions as a cause for increased seepage concentrations; however, their application may require additional hydrology data and chemistry data from the preimpoundment aquifer—the *end member* sample data (Freeze and Cherry, 1979). This information is not always available, and drilling and well development may be required to obtain it.

Calculation Rules

Next, as a set of calculation rules are developed for the proposed reactions and possible mixing processes. The calculation rules can be implemented in a computer spreadsheet, and should prioritize reactions for constituents having a unique cause and associated reaction, such as loss of Na^+ from cation exchange, before changes having several possible causes and associated chemical reactions are calculated. The coefficients used in the calculation rules are obtained directly from the balanced chemical reactions thought to account for the difference data. The following example shows that other unique causes for changes in Ca^{2+} and HCO_3^- must be accounted for in the mass balance rules before calcite dissolution can be estimated:

1. **DO: aerobic bacterial respiration of dissolved oxygen** (equation 9)
   Rule: Assume all loss in DO is due to bacterial respiration. Calculate change in DO depending on differences in sulfate. If the seepage chemistry indicates a loss of sulfate during transit, assume anaerobic conditions and set seepage DO = 0. Use field DO values if seepage indicates no loss or a slight gain in sulfate.
   Input: $_{DO}$
   Output: DOC = -[0.7692($_{DO}$)]
   HCO_3^- = +[0.769($_{DO}$)]
   H^+ = +[1.111($_{DO}$)]

2. **Sulfate: reduction of sulfate to sulfide by anaerobes** (equation 14)
   Rule: Assume sulfate reduction if $_{SO4} < 0$; otherwise enter 0's under input/output columns.
   Input: $_{SO4}$, only if NEGATIVE
   Output: DOC = -[2.0($_{SO4}$)]
   HCO_3^- = +[2.0($_{SO4}$)]
   H^+ = +[H($_{SO4}$ x 10^{-7})]

3. **K-Feldspar: incongruent dissolution of orthoclase** (equation 7)
   Rule: Assume K-feldspar weathering to kaolinite if $_K > 0$; otherwise enter 0's under input/output columns.
   Input: $_K$, only if POSITIVE
   Output: HCO_3^- = +($_K$)
   SiO_2 = +[2.0($_K$)]

4. **Na-exchange: monovalent cation exchange on smectite**
   Rule: Assume cation exchange if $_{Na}$ and/or $_K < 0$; otherwise enter 0's under input/output columns.
   Input: $_{Na}$ and/or $_K$, only if NEGATIVE
   Output: Ca^{2+} = +[2.0($_{Na}$ + $_K$)]

5. **Calcite: congruent dissolution of calcite** (equation 5a)
   Rule: Assume calcite dissolution if $'Ca > 0$ after being adjusted for Ca from cation exchange(6); otherwise enter 0's under input/output columns.
   Input: $'Ca$, where $'Ca = Ca - [Ca^{2+}]_{Exchange(4)}$
   Output: Mg^{2+} = +[0.239($'Ca$)]
   HCO_3^- = +[2.478($'Ca$)]

Note that contributions of Ca^{2+} from rule 4 (ion exchange), and HCO_3^- from rules 1, 2, and 3 (biotic processes and incongruent dissolution), must be accounted for before the remaining Ca ($'Ca$) can be used to estimate the amount of calcite dissolved using rule 5. Next, the set of calculation rules is translated to a spreadsheet for performing the mass balance calculations.

Ideally, the sum of all the mass balance reaction products in the spreadsheet should equal the observed changes in the seepage chemistry as seen in the set of difference data. In the real world, perfect mass balance is not always possible because of the complexity of dam seepage, the potential for isolated mineral occurrences, unique conditions along seepage paths, and the inherent uncertainty of sample collection and analytical chemistry measurements.

Table 5a shows an example of a calculation grid used for a mass balance model developed at Deer Flat Embankments (Craft, 1989). This example demonstrates how a mass balance model suggests that many changes in seepage concentration are not caused by mineral dissolution. Table 5b is a summary of mass balance

Table 5a.—An example mass balance calculation sheet for Deer Flat Embankments, Lower Embankment—Weir 4 on 4-25-88. In the top row of data are the total changes ( )$_i$) in concentrations in mmol/L observed between seep and reservoir. Beneath this row are the geochemical and biotic processes (balanced chemical reactions, 1-11) thought to be responsible for the observed changes in seepage concentrations—all arranged in priority computational order. The associated contributions to the mass balance are calculated in each of the table cells associated with a particular reaction, and then summed at the bottom of the table.

Constituent	DO	DOC	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	SO_4^{2-}	Cl^{-}	SiO_2	H^{+}
)$_i$ mmol/L	-0.312	-0.188	+0.175	+0.550	-0.1	0	+2.08	-0.235	-0.06	+.920	+2.40*
1. DO	-0.312	-0.24					+0.240				+0.347*
2. Sulfate		-0.47					+0.470	-0.235			0
3. Halite					0				0		
4. K-Feldspar						0	0			0	
5. Oligoclase			0		0		0			0	0
6. Na-exchange			+0.050		-0.1	0					
7. Calcite			+0.170	+0.041			+0.421				
8. Mg-Silicate			+0.153	+0.509						+0.611	-0.153*
9. Kaolinite			-0.153							-1.22	+0.306*
10. Silica										+1.60	
11. Anaerobic		-1.10					+0.944				+1.29*
BALANCE	*0*	*-1.62*	*0*	*0*	*0*	*0*	*0*	*0*	*-0.060*	*0*	*1.79**

* multiply these values by 10^{-8}

.

Table 5b.—Mass balance summary for 1988 Weir 4 seepage waters at Deer Flat Embankments. This includes the percentages of total soluble ion increases due to biotic processes, incongruent dissolution, congruent dissolution, and cation exchange (Craft, 1989).

Sample date	4-25-88	6-30-88	7-26-88	8-31-88
Reservoir elevation, m	769.01	767.91	766.82	766.24
Seepage flow, L/m	957.3	833.5	648.4	550.0
Biotic processes				
mg/L	99.2	97.3	90.9	95.8
weight percent	56.6	50.3	47.2	52.7
Cation exchange				
mg/L	2.00	0.002	0.200	0.200
weight percent	1.14	---	0.100	0.110
Incongruent dissolution				
mg/L	0	38.9	37.2	32.1
weight percent	0	20.1	19.3	17.7
Congruent dissolution				
mg/L	74.1	57.4	64.3	53.7
weight percent	42.3	29.7	33.4	29.5
Total increase				
mg/L	175	194	193	182
Total dissolution				
mg/L	74.1	96.3	102	85.8
weight percent	42.3	49.8	52.7	47.2

results where the dominant processes are summarized for the Deer Flat Embankments study. While this mass balance model may seem complicated, keep in mind that it attempts to account for minor changes in concentrations, and often a much simpler conceptual model (e.g., gypsum, calcite and biotic processes only) can be applied to get the same general results (Craft and Pearson, 2002).

Flow-Weighted Mass Wasting and Void Formation Calculations

Only after a mass balance model has estimated the percentage of increase in seepage concentrations caused by mineral dissolution processes should flow-weighted mass wasting and void formation estimates be calculated. These data can only be estimated for surface seeps with reliable flow measurements, and need to be compared to an estimate of seepage *contact volume* in the structure, foundation, or abutment. Contact volume is a difficult variable to quantify, so geophysical methods may be needed to provide accurate estimates. Also, because samples are collected at specific times, the flow-mass loadings must be seen as *instantaneous* values associated only with the sampling flow.

Flow-weighted loadings and estimated dissolution void volume rates should be calculated for seepage outfalls with flow data using procedures described by Bartholomew and Murray (1985). Example calculations may be found in appendix 3. The following summarizes the general approach for calculating seepage mass wasting and void formation volumes:

1. Net increase in seepage: For each analyzed constituent, same-date reservoir mg/L is subtracted from seepage mg/L to calculate net difference mg/L. Overall net difference was calculated by subtracting reservoir mg/L sum of ions from seepage mg/L sum of ions.

   $mg/L_{seepage} - mg/L_{reservoir} = mg/L_{net}$

   Sum of ions = $(Ca + Mg + Na + K + HCO_3^- + CO_3^{2-} + OH^- + SO_4^{2-} + Cl^- + Al + Fe + Mn + Si)$, mg/L

   Trace elements (Al, Fe, Mn, Si) reported below detection limits should be re-coded as one-half the reported limit of detection before net mg/L are calculated.

2. Simplified geochemical model: A mass balance model consistent with the observed geology and seepage chemistry should be developed, and the percentage of increase in seepage concentrations must be estimated.

3. Mass loading calculation, kg/day:

   $(mg/L_{net}) \times$ (seepage flow, ft^3/s) $\times$ (86,400 s/day) $\times$ (28.3169 L/ft^3) $\times$ (1.0×10^{-6} kg/mg)

   or

   $(mg/L_{net}) \times$ (seepage flow, gal/min) $\times$ (1,440 min/day) $\times$ (3.7854 L/gal) $\times$ (1.0×10^{-6} kg/mg)

4. Void volume formation calculation, m^3/day:

   m^3/day = ((mineral loading, kg/day)/(mineral density, kg/cm^3)) $\times$ 0.000001 m^3/cm^3

Table 6 shows mass wasting rate calculations derived from measured seepage and chemistry and a simplified mass balance model for Horsetooth Dam. This table also summarizes different potential void formation rates assuming different densities associated with anhydrite and gypsum.

Computer Groundwater Flow Models

Tools such as the MODFLOW model (McDonald and Harbaugh, 1988) are valuable for determining likely seepage flow patterns, seepage residence times in

Table 6.—Soluble mineral loading and void formation calculated from historical seepage chemistry and flow data at Horsetooth Dam (Craft, 1999)

Seep	Sample date	Flow, gal/min	Reservoir elevation, ft	Net loading as calcite, kg/d	Net loading as gypsum, kg/d	Net loading as anhydrite, kg/d	Gypsum + calcite void, m^3/yr	Anhydrite + calcite void, m^3/yr
EXSP-1	7/11/01	15.0	5353.5	5.21	-0.49	-0.39	0.571	0.600
EXSP-2	7/11/01	15.0	5353.5	5.46	-0.35	-0.28	0.623	0.644
SM-1	6/13/86	11.9	5414.3	3.51	0.06	0.04	0.444	0.441
	9/24/86	11.9	5376.5	4.34	0.61	0.48	0.633	0.597
	5/11/87	115.2	5414.1	43.17	2.97	2.35	5.820	5.65
	9/17/87	10.1	5397.5	3.86	0.24	0.19	0.516	0.501
	6/29/90	18.2	5407.8	5.56	0.17	0.14	0.716	0.706
	10/31/90	0.0	5390.4	0.00	0.00	0.00	0.00	0.00
	5/20/91	23.3	5423.2	6.99	0.33	0.26	0.918	0.899
	6/20/97	26.2	5423.3	9.66	0.18	0.15	1.23	1.22
	4/9/98	35.4	5426.6	11.68	0.50	0.39	1.53	1.50
	7/20/99	29.2	5428.3	9.55	0.27	0.22	1.23	1.21
	5/19/00	5.8	5389.8	1.28	0.44	0.35	0.226	0.201
SM-3	8/30/51	83.1	5353.2	72.48	27.30	21.58	13.2	11.6
	9/18/51	88.2	5355.3	63.23	28.14	22.25	12.2	10.6
	10/18/51	96.6	5358.6	77.15	29.01	22.94	14.0	12.4
	6/13/86	427.0	5414.3	135.59	8.01	6.34	18.1	17.6
	9/24/86	427.0	5376.5	108.82	80.15	63.38	25.9	21.2
	6/29/90	713.0	5407.8	126.33	140.52	111.12	37.3	29.2
	10/31/90	790.0	5390.4	146.43	166.82	131.91	43.9	34.2
	5/20/91	907.0	5423.2	131.03	144.71	114.43	38.6	30.2
	12/9/98	764.6	5380.3	100.04	89.70	70.93	26.2	21.1
	5/19/00	1068.6	5389.8	88.84	185.53	146.71	39.6	28.9
	5/9/01	496.6	5358.4	79.87	55.93	44.23	18.5	15.3
SM-7	10/31/90	673.0	5390.4	177.94	161.06	127.36	46.9	37.6
	5/20/91	978.0	5423.2	205.27	206.52	163.30	57.3	45.4
	4/9/98	1323.2	5426.6	86.56	0.00	0.00	10.7	10.7
SM-FD98-2	7/19/99	94.9	5428.1	10.48	0.00	0.00	1.30	1.30
	5/18/00	13.8	5389.5	1.13	0.00	0.00	0.140	0.140
SM-FD98-3	7/19/99	154.3	5428.1	15.35	0.00	0.00	1.91	1.91
	5/18/00	47.6	5389.5	2.98	0.00	0.00	0.370	0.370

abutments and foundation, and hydrologic responses to changing reservoir elevations and outlet works operations. MODFLOW has also been recognized as an established standard evidentiary tool in litigation, and ASTM has developed calibration standards for applying groundwater models (ASTM, 2002a). Often, changes in seepage chemistry depend directly on hydrologic factors. The MODFLOW model was applied during a seepage investigation at Glen Canyon Dam (Craft, 1992) and suggested that seepage emerging in the canyon downstream of the dam was likely higher concentration reservoir water traversing at depth in a wide arc around the abutments, rather than seepage indicating mineral dissolution and possible structural impairment.

Statistical Analyses

Regression or time-series analyses may be appropriate to evaluate historical trends in seepage chemistry data; however, these methods require adequate numbers of data points, and time series analysis requires uniform frequency data. Because many chemical variables are often measured, seepage chemistry may also be compared and analyzed using multivariate statistical methods like discriminate analysis, cluster analysis, or principal components analysis. Multivariate methods are best used to classify seepage into classes, and are more robust (less prone to normality and autoregression assumption violations) than regression and time series methods. While there are many statistics software packages available for use (SPSS, SAS, Systat), it is best to consult with an experienced statistician if the data analysis task is complicated.

Seepage Investigation Planning Guidelines

The variety of potential causes for seepage chemistry changes, the hydrologic complexity of seepage, and the heterogeneity of naturally occurring minerals make typical seepage studies complex endeavors that require quality data and the knowledge and skills of several different disciplines. The project manager should consider forming an interdisciplinary team with the following skills:

- *Analytical chemistry* is essential to specify the appropriate chemical tests, proper sample collection techniques, degree of quality assurance applied to the chemical data collection, and supervision and reporting of analytical tests. *Geochemistry* knowledge is needed to analyze the mineralogy, hydrology, and chemistry data to provide an assessment of potential dissolution from mineral-water interactions.

- *Hydrology* and *geophysics* are important to identify likely seepage flow paths and volumes, determine whether the reservoir-influenced aquifer is mixing

with any preimpoundment aquifer, selection of observation well or drill hole siting and sampling, and modeling of site groundwater flow using computer flow models.

- *Geology* and *petrography* are needed to properly identify the geology and mineralogy of materials in the foundation, abutments, and structures at the site. This knowledge is also critical to drilling programs and well installations where screens must be placed to intercept strata containing soluble minerals.

The following sections provide an outline of the issues that project managers should consider to properly evaluate seepage chemistry and mineral dissolution. Keep in mind that these recommendations reflect an ideal situation where resources and planning time are not limited. In a real situation it is not always possible to do all that is suggested here. It is important; however, to examine these issues and to develop a sound approach given the limitations inherent in field investigations.

The Sampling Plan or L-23 Document

A chemist should develop a sampling plan in consultation with project geologists, hydrologists, engineers, and field personnel. This sampling plan can be adapted with minor formatting as an official dam safety L-23 document providing instructions and guidance to field offices. Discussing the problem and developing such a plan ensures that *meaningful information* is obtained from chemical data and that the important questions are answered. This process also avoids selection of redundant or ambiguous sampling sites or wasting resources on overly frequent sampling. The sampling and analysis plan should address the following issues:

- *Definition of the problem*.—Despite seeming obvious, many times samples are collected without consideration of what the problem at a particular site might be. By defining this critical issue before sampling, informed choices for collection sites, chemical analyses, and appropriate data analysis can be made.

- *Review of pertinent background data*.—Before spending your budget on sampling and chemical analyses, locate as much existing data as practical and see what the existing data base suggests regarding the seepage problem.

- *Selection of seepage water sampling sites and chemical tests*.—After defining the problem and reviewing existing data, consider the following issues to define the chemical analyses:

    - *Sampling sites*.—Where are the obvious seepage problems, and how many sites need to be sampled to provide an adequate (technically and ethically sound) answer to the problem? What geologic formations

contain soluble minerals, and which observation wells and piezometers intercept these formations?

- *Sampling frequency*.—Does the reservoir experience large seasonal variations in water quality, reservoir surface elevation, or seepage flow? How often should samples be collected to ensure that chemical data correspond to the expected range of hydrologic conditions at the site throughout the year?

- *Required chemical analyses and field measurements*.—Several chemical and physical variables need to be measured in the field at the time of sampling.

- *Identify additional samples/tests*.—Chemical data are not the only variables that are important to seepage investigations. It is important to have good engineering, geology, and hydrology test data that may be compared with chemical data to draw sound conclusions regarding seepage. If historical data are not available, then additional tests may be needed:

  - *Additional drilling and coring*.—If original project geology is missing or spotty, additional core samples from abutments may be needed for physical properties and mineralogy testing. Wells should be developed and logged following standard procedures (ASTM, 2005a, 2005b, 2005h; EPA, 1975; Reclamation, 1981).

  - *Well testing and other hydrologic tests*.—If project hydrology is poorly understood, additional test wells or piezometers and aquifer testing may be needed to obtain local aquifer properties using slug tests or pumping tests (Freeze and Cherry, 1979), and following procedures established by Reclamation (1981), EPA (1975), and ASTM (2005a, 2005b, 2005h).

  - *Leaching tests*.—These tests simulate simple dissolution processes in earthen embankments by mixing reservoir water with soils representative of the structural materials. These sorts of tests on borrow area materials are a good simulation for first filling mineral dissolution behavior in a new dam, or when an embankment has been modified. Procedures for these tests have been published by the U.S. Department of Agriculture (USDA, 1953), the American Society of Agronomy and the Soil Science Society of America (ASA-SSSA, 1982, 1986), and the Canadian Soil Science Society (CSSS, 1993).

  - *Additional petrographic tests*.—If dissolution of specific minerals is suspected based on project geology information, mineralogy should be confirmed by additional petrographic tests. Suspended materials in

seepage outflows or precipitates may also be collected for petrographic identification.

- *Dye tracer studies*.—These tests involve use of fluorescent dyes, such as Rhodamine A, to determine or confirm underground flow paths. Very low concentrations of fluorescent dyes may be detected using a field fluorimeter. These tests can be very important if abutments or foundation lie in fractured or karst formations, or if seepage flow is high. Procedures have been established by ASTM International (ASTM) (ASTM, 2003a), the Environmental Protection Agency (EPA) (Quinlin, 1992) , and the U.S. Geological Survey (USGS) (Kilpatrick and Wilson, 1989), and several example studies performed in karst geology have been published (Mull, et al., 1988; Van Dike, 1985). Appendix 1 lists sources who perform dye testing.

- *Geophysical techniques*.—In the past 30 years, great strides have been made in underground void detection and flow detection methodologies. In almost every case, direct information concerning flow paths and voids is preferred. Methods such as microgravity (ASTM, 2005d; Rybakov, et al., 2001), electrical resistivity (ASTM, 2005e, 2005f, 2005g), and ground penetrating radar (Hoover, 2003) have been applied in diverse fields from petroleum prospecting to archaeology. Appendix 1 lists sources who perform geophysical testing.

- *Stable isotope mass spectrometry*.—This specialized analytical methodology has been used for oil exploration and groundwater and mixing evaluations for many years (Epstein and Myeda, 1953; Kaufman, et al., 1984; Desaulniers, et al., 1986; Long, et al., 1993) and may be applied to evaluate local aquifer and reservoir seepage mixing. Appendix 1 lists sources who provide stable isotope testing.

- *Quality control for chemical analyses*.—This is a critical issue that is often overlooked by nonchemists. The reliability of decisions based on chemical data often depend on the accuracy and precision of the analyses and the legal defensibility of the data. These variables cannot be evaluated without a plan to validate and document test results from analytical labs.

- *Data analysis and interpretation of data*.—The sampling plan should also address how the study data will be evaluated to provide *information* needed to solve the problem. This is an extension of the problem definition process. Because seepage investigations are often complex problems where geology, hydrology, and chemistry data must be related in a coherent manner, it is important to decide how data reduction and analysis tools should be applied at the beginning of the project.

- *Deadlines and funding commitments*.—Including these issues prevents misunderstandings that may arise regarding the scope of the investigation and critical deadlines for reporting results and analyzing the data. Often, data collection and interpretation activities must be limited due to funding shortages or emergency responses.

Selection of Sampling Types and Sites

It is important to collect water and solid samples that will provide data regarding initial and final conditions to adequately determine the relative contribution of processes affecting seepage chemistry. The following samples should be considered for collection:

- *Water samples from the reservoir (mandatory)*.—Reservoir data are needed to compare changes in seepage chemistry with initial conditions. These data are necessary to evaluate potential mineral dissolution and mixing hypotheses. If the reservoir is over 60 feet deep, it is also important to collect samples at multiple depths—especially near the reservoir bottom—due to chemical concentration gradients that may exist due to thermal or density stratification.

- *Water samples from active seeps (mandatory)*.—These are seepage emergence sites close to or located on the structures of concern at the dam. Select these sampling sites with care. Groundwater may be anaerobic, and the chemistry may quickly change when the sample is exposed to atmospheric oxygen. Collect seepage as close as possible to emergence points on the embankment, foundation, or abutments. If possible, install weirs and measure the seepage flow at collection sites during sampling.

- *Water samples from preimpoundment or "native" groundwater (if available)*.—Often, there are local aquifers that may mix with reservoir seepage at the dam site. Another potential scenario is that some seepage may encounter low permeability deposits where locally higher groundwater concentrations slowly leach into faster moving adjacent seepage paths. Mixing of the reservoir-influenced local groundwater with other aquifers and groundwaters may produce seepage concentration increases that mimic the effects of mineral dissolution. Data from native groundwater samples provide another set of initial concentrations that may be used to test a mixing hypothesis. These samples are sometimes available from wells at farms or ranches located away from the reservoir, but within the general project area.

- *Water samples from observation wells in abutments, foundation, or embankment (if available)*.—These samples provide a "view" of seepage water before it emerges at the surface as a leak and is exposed to atmospheric oxygen. They also provide *in situ* samples at the depth of seepage water in the formation or embankment zone of concern.

- *Water samples from structural drains and galleries*.—Samples collected at emergence points in drainage galleries and toe drains may provide clues regarding *where* possible chemical changes in seepage are occurring. Drainage flow data are also critical input for groundwater flow models, such as MODFLOW or MODPATH.

- *Water samples to avoid*.—Avoid water samples from surface ponds and catchments that collect seepage from several sources and are subject to surface runoff or evaporation. These are *ambiguous* sites because it is difficult to determine what mix of processes or water sources are responsible for changes observed in chemical concentrations. Water samples from drainage galleries should be collected as near as possible to the emergence point, before it has had a chance to mix with seepage from other source locations.

- *Solid samples from borrow areas*.—Borrow areas are an excellent place to collect samples of soil used for zone 1 and 2 materials in earthen embankments. Petrographic analyses of these samples help identify readily soluble minerals like gypsum or halite, and leaching chemistry tests may provide additional information regarding soluble minerals available under a simulation of reservoir "first filling" field conditions.

- *Solid samples from structures, abutments, and foundation*.—The petrography and physical properties of abutments and foundation are important to understand mineral-water interactions during seepage transit. Materials from the structure, both above and below the phreatic surface, provide important information relating to seepage transformations and potential flow paths. Leaching chemical tests of these geological materials may provide valuable information regarding seepage processes, and methods should conform to standards established by ASTM, ASA, and SSSA (ASA-SSSA, 1982, 1986).

- *Solid samples of any precipitates or deposits near seepage emergence points*.—Seepage chemical conditions often change rapidly upon emergence from structure, abutments, and foundation. These changes often result in precipitation of minerals, such as calcite, which appear as white deposits. Petrographic or chemical analysis of these deposits provide another clue to define the chemical processes active during seepage transit.

- *Solid samples of materials suspended in seepage flows*.—Suspended materials in seepage water outflows, usually visible as an opaque cloudiness, muddiness, or milkiness, should be collected for petrographic and/or chemical analysis. These suspended materials may be structural materials that suggest piping along seepage flow paths, or a chemical precipitate—not related to structural materials—caused by changes in seepage chemistry during structural transit. Because suspended materials may redissolve upon sitting in the seepage water, they should be separated from seepage water as

soon as possible using filtration or centrifugation on site. Enough water should be collected to provide an adequate solid sample for subsequent analysis. Petrographic tests are more important than chemical tests for suspended solids because the mineralogy of these materials may suggest that piping of dam structural materials is occurring—a potentially serious danger.

Timing and Consistency of Sample Collection

An important organizational aspect of any seepage investigation is consistency. It is critical to collect all seepage, drainage, reservoir, and well water samples within 2 to 3 days, and to consistently sample the same sites over time. Nomenclature for piezometers, wells and seeps often varies between designers, area office personnel, and irrigation districts. A single set of station identifiers should be used. These precautions ensure accurate comparisons of reservoir and seepage data on a given date, and over seasonal or annual cycles.

Field Measurements and Observations

The importance of accurate field observations when evaluating mineral dissolution cannot be underestimated**.** Samples from seeps and wells often exhibit significant changes in chemical concentrations when exposed to air or lower surface pressures, and sampling activities can alter conditions significantly. Because of these rapid changes, it is best (but not always practical) to measure several chemical constituents at the time of sampling. Developing an accurate mass balance model also depends on accuracy for comparing field pH, DO, turbidity, and Eh measurements. They provide important corroboration for chemical data and general evaluations of the extent or severity of a problem.

The person collecting or supervising the collection of samples should record field observations on log sheets or in a notebook. Forward copies of the field log sheets or notebook to the chemist assigned to analyze the data. Keep the field notebook as part of the project file. Include photographs and slides of all sampling sites in the project documentation file. When possible, measure or note the following at the time of sampling:

- Date, time, air temperature, general weather conditions
- Reservoir elevation
- Seepage flow rate or piezometer level prior to pumping or sampling
- Seepage and reservoir sample temperature, to ±0.2 °C
- pH and alkalinity (unless lab can analyze within 24 hr)
- DO using a modified Winkler titration, or a calibrated DO probe
- Presence of any notable odor at the sampling site, especially hydrogen sulfide (rotten egg) odor

- Presence and photographs of any mineral deposits in or around the seepage sampling site
- Any indication of piping or excessive suspended materials in seepage water
- Any other field observations pertinent to the problem
- If required, perform sample filtration in the field. Use a syringe fitted with a filter cartridge, or a pressure filtration apparatus.

Chemical Analyses for Water Samples

Table 7 summarizes the consensus methods that should be requested for seepage water sample analyses. Request the following chemical analyses when mineral dissolution is suspected as a problem at a dam site:

- Major ions, including sodium, potassium, calcium, magnesium, sulfate, chloride, carbonate, bicarbonate, and, if pH is >10, hydroxide
- Lab pH, conductivity, and TDS—filterable residue (180 °C)
- Trace metals: iron, manganese, and aluminum
- Silica as SiO_2 (may also be analyzed as a trace metal)
- Total and Dissolved Organic Carbon (TOC/DOC)—requires a separate sample bottle, and may be advisable if biological processes are suspected to influence the seepage chemistry at the dam

The author highly recommends that seepage chemistry team members obtain access to a copy of *Standard Methods for the Examination of Water and Wastewater* (APHA, AWWA, WEF, 1998), usually just called *Standard Methods*. This is the single most valuable source of information on analytical methodology, and it is used and cited by almost all analytical laboratories. Another good sources of information is Wagner's *Guide to Environmental Analytical Methods* (1998), which provides cross reference tables for EPA and *Standard Methods* method numbers.

Quality Assurance (QA) and Quality Control (QC) for Seepage Studies

QA is the name given to a set of procedures that specify overall project data quality, including sampling procedures, requirements for chemical analysis quality reporting and evaluation, and final purpose and intended use of results (Taylor, 1987). QA includes problem definition, sample site selection, frequency of sampling, sampling procedures, chemical analysis quality, as well as final data

Table 7.—Acceptable consensus methods for chemical analyses to cite on sample submittal or chain of custody forms

Analyte	Analytical technique	Standard methods numbers	EPA method numbers	Required detection limits, mg/L
Ca^{2+}-Mg^{2+}-Na^{+} -K^{+}	ICP-ES ICP-MS AAS	3120 3125 3111	200.7 200.8 215.1- 242.1 273.1- 258.1	0.25
Ca^{2+}-Mg^{2+} Na^{+}-K^{+}	EDTA Titration Flame Photometry	3500-Ca 3500-Na, 3500-K	- -	1.00 0.25
SO_4^{2-}, Cl^{-}	IC	4110	300	0.5
HCO_3^{-}, CO_3^{2-}, OH^{-}	Titrimetry	2320	310.1	1.0
pH	Electrometric	4500-H^{+}	150.1	NA
EC	Potentiometric	2510	120.1	10 µS/cm
TDS	Gravimetric	2540-C	160.1	5
DOC	Combustion Oxidation	5310B 5310C	415.1 -	1.00 0.10
Fe-Mn-Al-Si	ICP-ES ICP-MS (not Si) GFAAS (not Si)	3120 3125 3113	200.7 200.8 236.1- 243.1 202.1	Fe-Mn 0.005 Si-Al 0.05
Silica - SiO_2	Colorimetric	4500-SiO_2D		0.05
NO_3+NO_2	FIA	4500-NO_3	352.1	0.01
NH_3	FIA	4500-NH_3	350.1	0.02
ON, N_{org}	FIA	4500-N_{org}	351.1	0.10
Total P	FIA	4500-P	365.2	0.005
Ortho-P	FIA	4500-P	365.1	0.005

ICP-ES = Inductively Coupled Plasma Emission Spectrometry
ICP-MS = Inductively Coupled Plasma Mass Spectrometry
IC = Ion Chromatography
FAAS = Flame Atomic Absorption Spectrometry
GFAAS = Graphite Furnace (Electrothermal) Atomic Absorption Spectrometry
FIA = Automated Flow-Injection or Segmented-Flow Colorimetric Analysis

analysis. QC is similar to QA except that QC usually refers only to the quality procedures and documentation used in the chemical analysis laboratory or a defined project activity. The *sampling plan* mentioned as the starting point for seepage chemistry investigations is actually a QA plan, and should address the issues summarized as follows.

Proper Sampling Methods

While most projects involving chemical measurements tend to weight QA scrutiny toward the chemical analysis laboratory, the single greatest factors affecting data quality involve sampling representativeness and contamination *in the field*. Given the background costs associated with well development, piezometer installation and monitoring, and weir installation and monitoring, the greatest costs for seepage analyses are also associated with sample collection activities. So, it makes sense to include sampling QA as an integral part of any seepage study.

While most water samples are homogeneous, any water containing suspended materials is not. Contamination through lack of cleanliness or use of improper procedures and equipment can render analysis results useless. Sampling plans should reference consensus procedures promulgated by EPA (1981, 1982), USGS (1995), ASTM (1992, 2005c), and ASA-SSSA (1982, 1986), and field personnel should have written procedures, training, and audits to ensure that these procedures are followed.

Solid materials in dams and borrow areas are not homogeneous with respect to chemical and mineralogical properties, and some thought must be given to how solid samples are to be collected. *Simple grab samples, especially for characterizing large deposits of material, are not recommended.* A relatively simple approach for obtaining a representative solid sample is to collect and prepare composite samples. The fractional spooning method, as suggested by Gy (Pitard, 1993; Ramsey, 1998) is a robust way of collecting composite samples and identifying sources of error.

Laboratory QA/QC Plan

Many laboratories now have QC programs and are able to provide data quality reports with the requested analysis results. A laboratory QC plan provides information regarding analysis methodology, instrument standards and calibration, and analysis checks for precision and accuracy. Do not send samples to labs that do not have a well defined QC program. The best labs follow what are called *continuous improvement* quality plans such as those defined by the American National Standards Institute (ANSI) (ANSI-ASQC, 1991), the International Standards Organization (ISO) (ISO-IEC, 1990) or ASTM (2001, 2002b, 2002c, 2003b, 2003c). These quality models require the lab to operate under a formal quality assurance plan (QAP), with written standard operating procedures (SOPs), calibration verification, statistical control charting, corrective action documentation, maintenance documentation, a document control program, and auditable quality plans. Such quality plans can be certified by government agencies or organizations such as the American Association for Laboratory Accreditation (A2LA). In general, the seepage investigation project manager should consider the following QA activities to monitor analysis labs:

- *Laboratory audit and qualifier samples*.—Before samples are collected, it is a good idea to audit the laboratory chosen for chemical testing following guidelines consistent with ASTM standards (ASTM, 2001, 2002c, 2003c). This process may involve a visit and formal evaluation, review of interlaboratory "round-robin" sample analysis program participation (ASTM, 2002b; 2003c), or submission of QA qualifier samples that the proposed lab must correctly analyze.

- *Blind QA samples*.—The problem with laboratory QC programs, however, is that they do not always guarantee quality analyses. Depending on the study requirements, submit all or some of the following special blind QA samples (called *blind* because the QA samples' true identity is concealed and the analysis lab thinks that these samples are regular samples) along with the regular seepage and reservoir samples to provide an independent check of analysis quality and laboratory performance:

    - *Duplicates*.—Submit approximately 5 percent of the samples normally collected as concealed or "blind" duplicates. This means that you should collect two samples at randomly selected sites and assign one of the samples an identifier other than "Duplicate". For example, if wells 1 through 10 are real samples, you might call the duplicate "Well 11." If the analysis results for the duplicates vary beyond expected precision limits (use ±5 percent for major ions results, ±10 percent for trace elements), then the data may be unacceptable. This precaution also allows you to request reanalysis for chemical constituents having poor precision.

    - *Blind check samples*.—A check sample is a certified standard water having known component concentrations. These samples are available from commercial sources (see app. 1) for a variety of chemical constituents, and usually provide true values and acceptance ranges to judge results. Compare the lab results to the known value to assess analysis *accuracy*. Like the duplicate samples, submit check samples as blinds with sample identifiers that simulate real samples (e.g., "Well 12").

    - *Field blanks*.—These samples contain deionized water, poured into sample bottles at the dam site. Submit field blanks as blinds. Field blank results indicate whether contamination may be influencing results; however, they cannot distinguish between contamination occurring in the field or the analysis laboratory.

Evaluating Existing or Contract Data Quality

Sometimes samples are collected and analyzed without the benefit of a formalized sample plan. If major ions analyses were performed, it is still possible to evaluate overall analysis quality using the following criteria as summarized in *Standard*

Methods (APHA- AWWA-WEF, 1998). The calculations may be done manually, or performed in conjunction with a chemical equilibrium model run.

1. *Cation/anion balance*.—All natural waters are electroneutral, and cations and anions should be present in equal milliequivalent per liter (meq/L) concentrations. Calculate cation/anion balance as a percentage for samples *where all major ions are reported* using the following formula:

$$\frac{\left(\sum \text{cations, meq/L}\right)-\left(\sum \text{anions, meq/L}\right)}{\left(\sum \text{cations, meq/L}\right)+\left(\sum \text{anions, meq/L}\right)}\times 100$$

   Acceptable limits for cation/anion balance percentage vary depending on the total concentration of the water samples. Acceptable values are usually within ±5 percent. Positive values indicate cations may be in excess (or anions in deficiency); negative values indicate excess anions (or cations in deficiency). Cation/anion balance is calculated routinely with the WATEQ4F and MINTEQ models.

2. *Measured Total Dissolved Solids (TDS) vs. calculated TDS*.—Filterable residue should equal (or exceed) the sum of major ions in mg/L from the analysis results. The calculation and acceptable range are:

$$1.0 < \frac{\text{Measured TDS, mg/L}}{\text{Calculated TDS, mg/L}} < 1.2$$

   Low values for this ratio suggest that the filterable residue determination is in error (loss of sample aliquot), or that one or more measured ion concentrations are erroneously high. High ratios may suggest incomplete evaporation of residue, or erroneously low ion concentrations. High values may also be acceptable, given that not all potential residue constituents are analyzed.

3. *Calculated conductivity (EC) vs. measured EC*.—The EC calculated from the individual ion data should correspond to the measured value. The calculation and acceptable range are as follows:

$$0.9 < \frac{\text{Calculated EC, } \mu\text{S/cm}}{\text{Measured EC, } \mu\text{S/cm}} < 1.1$$

   Ratios outside the acceptable range may be due to improper conductivity measurement, or erroneous constituent ion concentrations. This test is more applicable to low concentration samples because high ion concentrations encourage ion-ion interactions that reduce ion-mediated electrical conduction. The MINTEQA2 model provides a comparison of theoretical vs. measured EC.

Procedures for Collecting Dam Seepage Water Samples

Use the following procedures to collect seepage and other water samples for chemical analyses during dam safety investigations. Coolers and "Blue Ice" are available from retail sporting goods outlets. Certified clean sample containers are available from several commercial sources (app. 1).

Containers

Collect samples for different tests in separate bottles and use clean sample bottles. Precleaned and certified sample bottles are available from commercial sources—see appendix 1 for sample bottle sources. Refer to *Standard Methods* (APHA-AWWA-WEF, 1998) for recommended holding times, preservation method, and sample containers. Use the following guide depending on the tests to be performed:

- *Major ions (Na, K, Ca, Mg, Cl, sulfate, alkalinity, conductivity, residue).*—Use wide-mouth, 500-mL to 1-liter, deionized-water-cleaned high density polyethylene (HDPE) bottles. Do not filter the major ions sample.

- *Trace elements (Fe, Mn, Al, Si, or other elements).*—Use 250- to 500-mL nitric acid/deionized-water-cleaned HDPE bottles. Filtration onsite generally risks potential contamination, so it is best to have the analytical lab filter the raw, unpreserved samples on receipt. If onsite filtration is required, filter through a 0.45-µm pore-size membrane filter using a syringe filter cartridge and introduce the filtered water directly into certified clean sample bottles containing nitric acid preservative. Certified clean bottles containing recommended amounts of preservative nitric acid are commercially available.

- *TOC/DOC.*—Use a deionized-water-rinsed, 500-mL amber glass bottle. If DOC is needed, perform filtration at the sampling site or have the analytical lab filter the raw, unpreserved samples on receipt.

- *Other tests.*—Consult with your analytical lab for assistance with container selection for other tests.

Cleanliness

Avoid contaminating the sample. Make sure that hands are clean prior to collecting samples, and take precautions to prevent contamination of the sample with sweat, skin oils, caliche or salt deposits, or dust and dirt at the site. Clean sampling equipment and rinse with deionized (distilled) water in between sampling sites. In very dirty environments, use disposable plastic clean room gloves and discard gloves after each station is sampled.

Rinse Bottle with Sample

Unless sample volume is severely limited or groundwater is anaerobic, rinse the major ions and TOC/DOC sample bottle three times with the sample before filling the container. A minimum volume of 10 mL per wash is adequate to rinse a 1-liter bottle. Add the wash water, seal the bottle, shake vigorously, and then discard the wash water. If nitric acid preservative is in the bottle, samples for trace elements should be collected without rinsing the sample bottle.

Collection Technique

Collect the grab sample by filling the sample bottle to overflowing and then screw the lid on tightly. Here are the common sampling situations and suggested procedures at a dam site:

- *Flowing discharge*.—This could be a pressurized seepage effluent or a drainage pipe. Hold the bottle in the flow path and allow the water to overflow the sample bottle before securing the lid. If the discharge flow rate is too high to hold the container in the flow path, you may need to improvise. Perhaps a small diameter plastic tube may be inserted in the flow to siphon a sample into the bottle. Use caution! If discharge flow is too high, you may need to move downstream and collect the sample when flow energy has subsided.

- *Difficult access sampling*.—For seepage discharges with difficult access, it is often possible to use a clean plastic bucket on a rope to collect water. Rinse and fill the sample bottle with the water in the bucket using surface water sampling procedures.

- *Reservoir surface or surface water sites*.—Submerge the sample bottle mouth beneath the water surface to fill. For shallow surface water collection, avoid stirring up bottom sediments during rinsing and filling.

- *Reservoir at depth*.—If sampling at depth is required, use a Van Dorn or Kimmerer style sampling device. Water column profiles are highly recommended if at-depth samples are collected. Use a recently calibrated

water quality multiprobe such as a YSI, Hydrolab, or In Situ model to measure depth profiles for pH, temperature, dissolved oxygen, conductivity, turbidity, and redox potential. See appendix 1 for commercial sources.

- *Low flow/volume seepage sites*.—Use a clean plastic punch bowl ladle to transfer seepage water to the sample bottle. Alternately, you may also use a large plastic syringe (50- to 100-mL capacity) fitted with an in-line filter cartridge to collect low volume seepage. Use a disposable polycarbonate membrane filter cartridge with a 0.45-µM pore size.

- *Drill hole or observation well*.—Refer to appendix 4 for a pictorial guide to procedures for water sampling from piezometer wells. Standard procedures applicable to well sampling include those from ASTM (2005c), and EPA (1981). Pump or bail the well depending on available equipment at the site and the nature of the well and the surrounding formation. It is very important to ensure that the water in the well is representative of the surrounding formation groundwater (Barcelona, et al., 1985). This is usually accomplished by emptying the hole and allowing it to refill several times, or by pumping for a period of time before collecting the sample. You may need to improvise procedures at the site, so it is important to record how the observation well samples are collected. *To avoid cross contamination of well samples, always clean sampling devices and rinse with deionized water before sampling a new well.*

    - If the formation is permeable, the well should be pumped until a minimum of five well volumes have cleared the outlet before sampling. A more stringent approach would be to monitor the conductivity of the pump effluent and pump the well until constant conductivity is observed.

    - In a low permeability (tight) formation, this approach may not be feasible. Remove stagnant water in a well by bailing or using a pressurized air hose lowered into the hole to “blow out” the well. After purging and refilling several times, collect the sample using a bailer. It may take an extended time for low permeability wells to refill, and this may cause extra inconvenience.

    - If the groundwater is anaerobic (it usually has a stinking rotten egg odor), special precautions may be needed to collect and preserve a sample before mixing with atmospheric oxygen.

- *Collection of suspended sediments in outflow*.—If a seepage outflow contains obvious suspended materials and has a cloudy or opaque appearance, it may be wise to collect a seepage sample for suspended materials. However, suspended materials sampling may be complicated, and it is recommended that sampling be preceded by consultation. In general, the

seepage containing suspended materials should be collected so that the *suspended material* is present in sufficient quantity for petrographic examination (usually 1-2 grams, minimum).

- If the seepage flow is highly turbid, a 3- to 5-liter sample volume (around a gallon) may be sufficient, but seepage with only slight turbidity may present a problem. Separating the suspended solid materials from the seepage water on low turbidity samples may increase laboratory costs, so that these issues should be discussed with the analysis laboratory before sample collection.

- Another consideration involves the standard water test for total suspended solids, or TSS. *DO NOT request this test.* Routine TSS (EPA Method 160.2 or *Standard Methods* 2540-D) is intended for water treatment plants and does not filter small clay-sized particles common to muddy and turbid seepage flows. If some measure of suspended materials is required, special provisions should be discussed with the analysis lab. These could involve nonroutine tests involving filtration through a 0.45-µm pore-size membrane, or centrifugation. Finally, low flow-rate turbid seepage may be heterogeneous, so care should be taken to collect a representative sample if suspended materials need to be quantified.

- Another approach that may be applicable to turbid outflows and toe drains is the installation of settling troughs that allow solids to settle and be conveniently collected, or installation of sediment capture bags that use fine mesh screen material to retain solids.

Sample Labels

After collecting the sample, CLEARLY label the container with sample identification information using a permanent, waterproof marker. Include the sample station, location, depth, well number, date, time, reservoir elevation, seepage flow rate, sample collector's name, sample pretreatment/preservation performed and analysis request. Include "DAM SAFETY" in the comments portion of the label. Most commercially available certified clean sample bottles are supplied with adhesive labels. Be sure to indicate if the sample is RAW, or unfiltered and unpreserved. Since labled samples will be placed in a cooler with ice, it is important to place each sample in a zip-lock plastic bag to prevent melt water from removing or disfiguring labels.

Sample Treatment—Filtration and Preservation

Perform sample filtration in the field only if judged necessary by the project chemist. Follow procedures outlined in *Standrd Methods* (APHA-AWWAP-

WEF, 1998) or the EPA (EPA, 1982). Use a syringe fitted with a filter cartridge, or a pressure filtration apparatus. Add ultrapure nitric acid (1 mL per liter of sample) to trace metal samples after filtration, or else make arrangements for the testing lab to handle filtration and preservation when samples are delivered.

Field Observations and Measurements

It is *VERY* important to note and record any significant observations when collecting samples. Field observations should be recorded in a *notebook* by the person collecting or supervising the collection of samples. Forward the field notebook information to the person assigned to analyze the data. If possible, include the following information:

- Date, time, air temperature, general weather conditions
- Reservoir elevation
- Seepage flow rate
- Seepage and reservoir sample temperature, to ±0.2°C
- pH and alkalinity (unless lab can analyze within 24 hr)
- DO, using a modified Winkler titration, or a calibrated DO probe
- Presence of any notable odor at the sampling site, especially hydrogen sulfide (rotten egg) odor
- Presence of any precipitated deposits in or around the seepage sampling site
- Any indication of piping or excessive suspended materials in seepage water
- Any other field observations pertinent to the problem
- If required, perform sample filtration in the field. Use a syringe fitted with a filter cartridge, or a pressure filtration apparatus.

Analysis Request Sheet or Chain of Custody Form

Fill out and include an analysis request sheet or chain of custody form (examples in app. 1) *with the samples* that lists the sample identifiers, the requested chemical analyses, priority, and charge account numbers. If the data will be used as court evidence, follow sample custody procedures and documentation outlined by EPA (EPA, 1986) or ASTM (ASTM, 2004). Note whether the sample is raw, filtered

and unpreserved, or filtered and preserved. Request the following chemical analyses:

- *Major ions*.—Sodium, potassium, calcium, magnesium, sulfate, chloride, carbonate, and bicarbonate, pH, conductivity, and filterable residue, 180 °C (also known as total dissolved solids, or TDS)

- *Trace elements*.—Iron, manganese, silicon, and aluminum on a *filtered* and *acidified* subsample. If filtration and preservation are not performed in the field, then have the analytical lab perform this prep work upon sample receipt.

- Other specific analyses (such as TOC/DOC or 0.45-µm suspended solids) as required (may require separate sample bottles)

Shipping

As soon as possible, store the labeled samples in a picnic cooler. Use prefrozen sealed "Blue Ice" cartridges to chill the cooler and samples. If loose picnic ice is used to chill the samples, seal the sample bottles and analysis request sheets in large Zip-Loc freezer storage bags. If legally defensible data will be required, blue ice is not acceptable, and documentation of sample temperature during shipping may be required. Ship the samples OVERNIGHT EXPRESS directly to the contract lab (see app. 1 for a list of analytical service labs).

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Appendix 1

Field Sampling Resources: Sample Submittal and Chain of Custody Forms, Sources for Field and Sampling Equipment, and Sources for Analytical and Technical Services

SAMPLE SUBMITTAL REQUEST FORM SHEET 1 of ____

U.S. Department of the Interior - Bureau of Reclamation

Project Name: _____

Today's Date: _____ Report Data by:_____

Samples Submitted By: _____ Telephone:_____

Mailing Address: _____ E-mail: _____

Sample Collection Location: _____ Sample Collected by:_____

Sampling Date(s):_____ Type of Samples:_____ Number of Samples:_____

Samples Filtered?_____ Samples Preserved?_____ (describe) Custody Form Required?_____

Final Data Report To:_____ QC Report Requested? **Yes**

Special Instructions: _____

SAMPLE IDENTIFIERS	*Requested Analyses*	*Method or Det Lim*
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
9.		
10.		
11.		
12.		
13.		
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15.		
16.		
17.		
18.		

ATTACH ADDITIONAL LIST FOR MORE SAMPLES

ATTACH CHAIN OF CUSTODY FORMS IF REQUIRED

Revised 07/05/2005

SAMPLE SUBMITTAL REQUEST FORM (Continued) SHEET____ of ____

U.S. Department of the Interior - Bureau of Reclamation

Samples Submitted By:_____ Today's date:_____

SAMPLE IDENTIFIERS	*Requested Analyses*	*Method or Det Lim*

ATTACH ADDITIONAL LIST FOR MORE SAMPLES

ATTACH CHAIN OF CUSTODY FORMS IF REQUIRED

Revised 07-05-2005

Calibration Standards and Reference Material Sources

Company	Phone	Website	Certification* notes
Absolute Standards	800-368-1131	http://www.absolute standards.com/	EPA-CRADA
AccuStandard	800-442-5290	http://www.accu standard.com/	A2LA
Analytical Products Group	800-272-4442 740-423-4200	http://www.apgqa.com/	ISO 9001 round robin audit program
ChemService	800-452-9994 215-692-3026	http://www.medibix. com/company/	A2LA
Environmental Resource Associates	800-372-0122 303-431-8454	http://www.eraqc.com/	A2LA blind QC samples for inorganics
High Purity Standards	843-767-7900	http://www.hps.com/	NIST—traceable EPA-CRADA
NIST	301-975-6776	http://www.nist.gov/	Primary Standards
Troemner, Inc.	800-352-7705	http://www.troemner. com/	NIST—traceable standard weight calibration

***** A2LA is the American Association for Laboratory Accreditation. ISO is the International Organization for Standardization. NIST is the National Institute for Standards and Technology (formerly the National Bureau of Standards). CRADA standards are reference solutions previously distributed by EPA, but now prepared according to EPA protocols by contractors through Cooperative Research and Development Agreements (CRADA's). The best source for SRMs is NIST (although expensive) or an A2LA-accredited or ISO 9000-certified supplier, although any SRM or standard that is analyzed and certified as traceable to an NIST or other recognized national primary standard is suitable for calibration verification.

Field and Lab Equipment Sources

The following vendors accept government bankcard orders and provide supplies needed for seepage chemistry studies:

Chemicals and Lab Gear

VWR Scientific	Offices in Major Cities	1-800-932-5000
http://www.vwrsp.com/		303-371-0970
Fisher Scientific	Offices in Major Cities	1-800-766-7000
http://www.fishersci.com/		303-371-0888

Field Gear and Instruments, Water and Soil Samplers, Filtration Rigs, Bailers, Pumps:

Forestry Suppliers, Inc.	Jackson MS	1-800-647-5368
http://www.forestry-suppliers.com/		601-354-3565
Ben Meadows Company	Atlanta GA	1-800-241-6401
http://www.benmeadows.com/		770-455-0907
Wildco (Wildlife Supply)	Saginaw MI	1-800-799-8301
http://www.wildco.com/		517-799-8100
Envirotech	Martinez CA	1-800-468-8921
http://www.envirotech.com/		510-370-1541
Hach Company	Loveland CO	1-800-227-4224
http://www.hach.com/		970-669-3050

Precleaned/Certified Sample Bottles:

Environmental Sampling Supply	Oakland CA	1-800-233-8425
http://www.essvial.com/		510-562-4988
Eagle Picher	Miami OK	1-800-331-7425
http://www.eaglepicher.com/		918-540-1507
I-CHEM	Hayward CA	1-800-443-1689
http://www.biobank.co.kr/maker/iii/ichem.shtmt/		415-782-3905

Fluorimeters:

Chelsea Technologies Group
55 Central Avenue, West Molesey, Surrey, KT8 2QZ, UK 44(0)2084819000
http://www.chelsea.co.uk/Instruments%20AQUAtracka.htm
Email: sales@chelsea.co.uk

Turner Biosystems
845 W. Maude Ave, Sunnyvale CA 94085 1-877-316-8049
http://www.turnerbiosystems.com 408-749-0994
E-mail: sales@turnerbiosystems.com

Analysis and Services Sources

Analytical Chemistry Labs:

Bill Stroud, Laboratory Manager, PN-3210
Bureau of Reclamation, Pacific Northwest Region
Regional Soil and Water Laboratory
300 East Garrison St. Boise ID 83702
bstroud@pn.usbr.gov 208-334-1540
fax 208-334-1858

Analytica
12189 Pennsylvania, Thornton CO 80241-3115 303-469-8868
http://www.analyticagroup.com/ael2/hael2.htm

Colorado Analytical Laboratory
240 S Main St., Brighton CO 80601-1614 303-659-2313

Hazen Research
4601 Indiana St., Golden CO 80403 303-279-4501
www.@hazenusa.com fax 303-278-1528

Huffman Laboratories Inc
4630 Indiana, Golden CO 80403-1849 303-278-4455
http://www.huffmanlabs.com/

National Testing Laboratories 1-800-458-3330

Paragon Analytics
225 Commerce Drive, Fort Collins CO 80524 970-490-1511
http://www.paragonlabs.com/ fax 970-490-1522

Severn Trent Laboratories Inc
4955 Yarrow St., Arvada CO 80002-4517 303-736-0100

Wyoming Analytical Labs Denver Division
1511 Washington Av., Golden CO 80401-0804 303-278-2446

Geophysics: Dye Tracers, Microgravity, Electrical Conductivity, Void Detection

Center for Cave and Karst Studies—Crawford Hydrology Laboratory
1 Big Red Way - EST 403, Bowling Green KY 42101 270-745-3252
http://www.dyetracing.com
http://caveandkarst.wku.edu

Enviroscan, Inc.
1051 Columbia Avenue, Lancaster PA 17603 717-396-8922
http://www.enviroscan.com

Maxwelton GeoSolutions, Ltd.
HC 40, Box 30-C, Lewisburg WV 24901 304-645-5359

Stable Isotope Mass Spectrometry

Geochron Laboratories
711 Concord Ave, Cambridge MA 02138-1002 617-876-3691
http://www.geochronlabs.com/contact.html

Water Sciences Laboratory—University of Nebraska, Lincoln
103 Natural Resources Hall, Lincoln NE 68583-0844 402- 472-7539
http://waterscience.unl.edu/isotope.htm

Water Analysis and Plotting Software

Rockware, Inc
2221 East Street, Golden CO 80401 303-278-3534
http://www.rockware.com/catalog/pages/aqqa.html

Rockware Aq-QA $199

Scientific Software Group
P.O. Box 708188, Sandy UT 84070-8188 +1 866 620 9214
http://www.ssgintl.com/aquachem_details/aquachem_details.html

AquaChem v. 5.0 $790
http://www.scientificsoftwaregroup.com/pages/product_info.php?products_id=129

MINTEQA2 for Windows $495
http://www.scientificsoftwaregroup.com/pages/product_info.php?products_id=196&sessid=5fad02c372c6fd0de13b3841158894c4

MINTEQA2-PRODEFA2 v. 4.02 free download (16-bit DOS application)
http://www.epa.gov/ceampubl/mmedia/minteq/

MODFLOW free download:
http://www.scientificsoftwaregroup.com/pages/product_info.php?products_id=172&sessid=462b18db152e20e749870325aea5ce4f

7-2518 (8-93)
Bureau of Reclamation

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DEPARTMENT OF THE INTERIOR

Chain of Custody Record

Project Manager	Project name	Batch identification

Sampled by and title (signatures)	Remarks	Initials and date sample destroyed
Laboratory		

Field identification	Date collected	Time	Lab identification	Sample type	Number of containers									Remarks	Initials and date sample destroyed

Relinquished by (signature)	Date	Time	Relinquished by (signature)	Date	Time	Relinquished by (signature)	Date	Time
Received by (signature)	Date	Time	Received by (signature)	Date	Time	Received by lab (signature)	Date	Time

Point of contact: _____

Remarks: _____

DISTRIBUTION: Original: Accompanies shipment. Pink copy: Field records. Yellow copy: Associate laboratory

Sample shipped via

☐ Priority Mail ☐ Bus ☐ Other

☐ Express Mail ☐ UPS

Appendix 2

Standard Operating Procedure: Running the MINTEQA2 Chemical Equilibrium Model

1. ***Summary:*** This Standard Operating Procedure describes how to install and use the MINTEQA2 chemical equilibrium computer program. Procedures are provided for setting up your computer, installing the program, entering data, running the model, and editing MINTEQA2 output files. This SOP is applicable for novice MINTEQA2 users who are running simple model simulations for typical water sample chemistry data.

2. ***Revision History****:* This SOP is an original 1.0 version.

3. ***Principal Reference:***

   3.1 Felmy, A.R., Girvin, D.C., and Jenne, E.A., *MINTEQ - A Computer Program for Calculating Aqueous Geochemical Equilibria*, USEPA, Environmental Research Laboratory, Athens GA, EPA-600/3-84-032, 1984.

   3.2 Allison, J.D., Brown, D.S., and K.J. Novo-Gradac, 1991. *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual*, EPA/600/3-91/021, U.S. Environmental Protection Agency, Environmental Research Laboratory, Office of Research and Development, Athens, Georgia.

4. ***Overview:*** MINTEQA2 (pronounced *min-tech*) is an MS-DOS computer program that calculates chemical equilibrium data for water samples based on measured concentrations of chemical components entered into the model. Components are measured chemical constituents, such as calcium, sulfate, alkalinity, pH, etc. MINTEQA2 calculates equilibrium *activity*, the thermodynamic version of concentration, for all forms (species) of a particular component, and saturation indices for all minerals that may have dissolved to form the water. This procedure gives the novice user directions on how to create a simple data file for a relatively direct MINTEQA2 run.

   4.1 This procedure is for running the MS-DOS version of MINTEQA2. You will need to open a DOS session under Windows in order to install the programs and data files needed to run MINTEQA2. If you are unsure about how to do this, consult your IT Help Desk. Once the files have been installed on your hard disk, you can create desktop shortcuts to run the *.exe programs. Open Windows Explorer, which is accessible through My Computer or the Taskbar Start Menu (right click on Program then select Explore). Find the MINTEQA2 folder on your C:\ drive. Find the file MINRUN.BAT, right-click on the file, and select “Create Shortcut.” Windows will recognize that this is a MS-DOS batch file and properly configure a way to run the program in a Window. Find the file PRODEFA2.BAT and create another shortcut as for the previous batch file.

   4.2 Analysis data are entered using another DOS program called PRODEFA2 (PROblem DEFinition). PRODEFA2 (pronounced *pro-def*) allows you to enter and edit measured chemical data for one sample (called a "problem" in MINTEQ), or multiple problems. Keep in mind that you will have to enter adjusted data for some components (such as alkalinity, arsenic, selenium) to

comply with how MINTEQA2 analyzes data. You may also enter and edit other variables that affect chemical equilibria, such as partial pressures of gases, redox potential, temperature, and pH. Finally, PRODEFA2 allows you to specify a *sweep* of one component's input concentration values that creates a multiple problem output file. This allows you to investigate "what if" situations where, for example, the general chemistry remains the same while a toxic pollutant increases in concentration, or the pH changes. When you exit PRODEFA2, the MINTEQA2 data file is saved under the name you supplied in a standard ASCII (text) file.

4.3 To run a problem, you first create and name a data file with PRODEFA2 that is stored on disk. You then run the MINTEQA2 program, which asks you for the input file name, and the output file name you want the results stored in. The model then executes, and if you have correctly specified the water chemistry, it will save the output in the data file name you entered. Both data and output files are simple ASCII text files that may be edited with any word processor, Windows WordPad, or Windows Notepad programs.

4.4 A Windows version of MINTEQA2 is available from Scientific Software Group, www.scientificsoftwaregroup.com, 1-866-620-9214.

5. ***Data Entry Conventions:*** In the following instructions, the DOS system prompt and program info requests are in normal `Courier font type`, while commands you will enter are in **`Courier boldface.`** Descriptions of entry choices are in *`Courier italics.`*

5.1 Specific keys to press are indicated by [brackets], such as [Enter], [Tab], [F2], etc. Almost all DOS and MINTEQA2 commands are followed by the [Enter] key. A [key] followed by a "+" and another [key] means "hold the first key down, press the second key, and then let go of both keys; for example [Ctrl]+[C], or [Alt]+[F].

5.2 Within the PRODEFA2 program, a [D] = "XX", for example, ([D]=Y) means that the default response is "XX", and may be selected by simply pressing [Enter]. "R" is a response option that will **R**eturn you to the previous menu screen. UPPER or lowercase letters may be used throughout PRODEFA2 and MINTEQA2.

5.3 If you get completely lost or have other problems, simply press [Ctrl]+[C] to abort the PRODEFA2 program and return to the DOS system prompt.

6. ***System Requirements:*** MINTEQA2 is a MS-DOS program and will run under most Windows operating systems. The MINTEQA2 model requires the ANSI.SYS driver file to be loaded in memory for the screen display to operate correctly. Consult with your IT Help group for assistance setting up shortcuts to correctly run MINTEQA2 and PRODEFA2.

7. ***MINTEQA2 Terms and Definitions:*** Here are a few MINTEQA2 terms and shoptalk you may encounter during data input or perusing MINTEQA2 output files.

Activity	*Activity* is the chemical equilibrium version of concentration that has been adjusted for ionic strength and temperature.
Charge Balance	In natural waters, positive and negative ions are present in equal concentrations (when expressed as equivalents/liter or milliequivalents/liter) and are thus electroneutral and *balanced*. MINTEQA2 will calculate charge balance as a percentage. Values close to zero indicate electroneutrality.
Component	a *component* is one of the master input variables for measured chemical constituents. Components are stored in the COMP.DBS file. Components are also called "Type I" species by MINTEQA2.
Ion, Cation, Anion	an *ion* is a chemical compound or element that has a positive or negative electrical charge, such as Ca^{2+}, or SO_4^{2-}. Charge is usually rendered as a superscript; however, MINTEQA2 runs in plain text mode, so charge is just concatenated to the end of the ion formula, such as FeOH+, CrO4-2. Positively charged ions are called *cations.* Negatively charged ions are called *anions.*
Problem	a *problem* is a data set for a single water sample that MINTEQA2 will use to perform equilibrium calculations. You can enter more than one problem in a data file.
Species	a *species* is a chemical compound formed from a reaction of one component with other components, or one of several oxidation states or charged ions for an element. $CaSO_4$ (aq), HCO_3^-, and $FeOH^+$ are examples of species formed from multiple components. Fe^{2+}, Fe^{3+}, and Cr^{3+}, Cr^{6+} represent oxidation-reduction (redox) species. Components are also species. Each component usually forms several species depending on the nature and concentrations of all the components in your sample.

8. ***Installation****:* MINTEQA2 is distributed on a floppy that contains a self-installing executable file called INSTALMT.EXE. To install MINTEQ, insert the self-installation disk into drive A:\, and execute the following commands at the DOS prompt:

8.1 If you are currently in Windows, exit Windows so that you see the DOS text screen and the system prompt (usually C:\, followed by subdirectory path names).

```
C:\> prompt $p$g [Enter]          This command says "display the
                                  current full subdirectory name
                                  and path as the system
                                  prompt".  If you didn't load
```

	this command on power-up in the autoexec.bat file, the prompt will only show: C>
`C:\subdir\subdir\>` **`cd\ [Enter]`**	*System pointer will move to the root directory, c:\, and will display the root directory prompt, C:\>*
`C:\>` **`a: [Enter]`**	*This says, "switch the system pointer to the A:\ disk drive."*
`A:\>` **`instalmt [Enter]`**	*Screen will clear and the install program will begin.*
`A:\>` **`C: [Enter]`**	*After installing, go back to the C:\ drive.*

8.2 From this point onward, you simply reply to the program's requests for information. Unless you want to experiment, select all default installation menu choices. The compressed files will be copied to your hard disk, usually into the C:\MINTEQA2 subdirectory. If there are problems de-compressing the MINTEQA2 files, you may need to copy those files from another computer that has the properly operating file to your hard disk. If you have problems, contact your local IT help staff.

8.3 Since almost all PCs now have plenty of memory, the fully installed version of MINTEQA2 and PRODEFA2, along with all data bases and subdirectories (folders), may be copied to a Zip drive or CD-ROM, and then copied to your local C: drive. MS-DOS shortcuts can then be used to run the model in DOS mode in Windows.

9. ***Creating MINTEQA2 Data Files:*** The PRODEFA2 program will create a properly formatted data file that you will "submit" to the MINTEQA2 program for analysis. The data file you create will be an ASCII text file that will be saved to disk (in the MINTEQA2 subdirectory) with the file name you define.

9.1 Before starting a series of MINTEQA2 runs, give some thought to how you will organize the data files and the names you will assign. Your file names are limited to 8 characters, plus a period and a 3-character extension. Name the data files in a logical way so that you will be able to identify them at a later date, and record the file names in a permanent logbook or notebook. I strongly recommend that you add the ***.dat*** extension to all data file names. Later, when you run the MINTEQA2 model, you should use the same file name for the output file, except use a ***.out*** extension to identify the files as model output.

9.2 In general, PRODEFA2 will present screen menus with numbered items for your selection choices. Selecting the number will call up a prompt asking you to enter the actual data. Default responses are indicated in the input prompt with a "[D]=" notation, such as (Y, N, [D]=Y). Simply pressing [Enter] will select the default

selection. After responding, you are returned to the screen menu. As you initially begin to use the PRODEFA2 program, take the extra time to read all the menu and screen instructions that appear during the entry process. PRODEFA2 uses several input screen menus it calls EDIT LEVELS.

9.3 The **MAIN MENU** (which ironically doesn't appear when you initially run PRODEFA2) allows you to select the different EDIT LEVELS for data input or review; create a multi-problem file with more than one sample; and to exit and save the data file you have created. **EDIT LEVEL I** is for entering general information about the problem (sample), such as titles, input units, temperature, pH, along with several MINTEQA2 run options. **EDIT LEVEL II** allows you to enter actual chemical data for your measured components data, as well as specify several other model analysis options such as including gases in equilibrium with the water sample, fixed redox species, adsorption simulations, and adding new species not in the MINTEQA2 data bases. **EDIT LEVEL III** will allow you to view and edit the data you entered under the LEVEL II menu. **EDIT LEVEL IV** will allow you to create a multiple problem file that will re-run the model while varying one component's concentration.

9.4 **Concentration Entry Conventions:** Before you start PRODEFA2, you will need to perform some data conversions to accommodate the peculiarities of MINTEQ. First, since most chemical analysis data from Lab reports is in mg/L (milligrams per liter) or :g/L (micrograms per liter), I recommend that mg/L units be selected. The following data conversions will need to be performed:

9.4.1 **Enter only DISSOLVED Concentrations:** Make sure that your ion and trace metal concentrations are not "total" data, were not digested, and were filtered prior to analysis. Don't get confused when running PRODEFA2 when it refers to TOTAL concentrations - it still means "dissolved".

9.4.2 **Convert :g/L to mg/L:** Trace metal results are often presented as :g/L; however, MINTEQA2 data must be entered as mg/L. Convert :g/L to mg/L by dividing :g/L by 1000.

```
Examples:
    6250 :g/L = 6.25     mg/L
     335 :g/L = 0.335    mg/L
    12.6 :g/L = 0.0126   mg/L
    2.56 :g/L = 0.00256  mg/L
   0.221 :g/L = 0.000221 mg/L
```

9.4.3 **Alkalinity, bicarbonate:** Enter all alkalinity data as carbonate, CO_3^{2-} (component #140, CO3-2). Here are the conversion factors to determine alkalinity as carbonate:

If you have multiply by

mg/L as Bicarbonate, HCO_3^-	0.49174
mg/L as Carbonate, CO_3^{2-}	1.000
mg/L as $CaCO_3$	0.5996

If you have alkalinity expressed separately as both carbonate and bicarbonate (for waters with pH > 8.3), perform the above calculations and add them together to calculate total alkalinity as carbonate. If you have alkalinity expressed as $CaCO_3$, you can ignore separate bicarbonate and carbonate data.

9.4.4 **Silicon:** Silicon data may be reported as elemental Si, or as SiO_2, silicon dioxide. MINTEQA2 requires Si input as $H_4SiO_4^0$ (component #770, H4SiO4). Convert Si data as follows:

If you have	multiply by
mg/L as Si	3.4222
mg/L as SiO_2	1.5997

9.4.5 **Arsenic:** Multiply mg/L as elemental As by **1.8946** to calculate mg/l as dissolved hydrogen arsenate, $H_3AsO_4^0$ (component #061, H3AsO4).

9.4.6 **Selenium:** Multiply mg/L as elemental Se by **1.8105** to calculate mg/l as selenate ion, SeO_4^{2-} (component #762, SeO4-2).

9.4.7 **Iron and Manganese**: For any water in equilibrium with the atmosphere, input Fe and Mn mg/L data as the oxidized forms Fe^{3+} (component #281, Fe+3), and Mn^{3+} (component #471, Mn+3). Both forms weigh the same, so no data correction is needed.

9.4.8 **Copper:** Input Cu as Cu^{2+} (component #231, Cu+2). Both forms weigh the same, so no data correction is needed.

9.4.9 **Concentration Data Below the Detection Limit:** Trace metal data are often non-detect values, usually listed as "ND" (for not detected), "NR" (for not reported), "UR" (unreported), "BDL" (below detection limit), or "<###" (less than reported detection limit, such as <0.001). In all of these cases, DO NOT enter zero concentration or enter the component into the data file. MINTEQA2 will not run properly if zero concentration is entered. On the other hand, you may wish to perform "what if?" simulations that have made-up concentrations below the instrument detection limit to see how the chemistry would change.

9.4.10 **Partial Pressures for Gases:** All surface waters are in contact with the atmosphere. The 2 gases most influential on water chemistry are carbon dioxide, CO_2 (species #3301403, CO2 (g)), and oxygen, O_2 (species

#3300021, O2 (g)). Concentrations for these gases are entered (via EDIT LEVEL II selection 4) as partial pressures - and these data vary with elevation above sea level. Partial pressures are notated as pO_2 and pCO_2. Enter the appropriate partial pressures from the following table:

Elevation, ft.	Partial Pressures, in atmospheres pO_2, atm	pCO_2, atm
0 (sea level)	0.2070	0.000326
5280 (Denver)	0.1741	0.000274
5640 (Fed Center)	0.1718	0.000271
10,400 (Leadville)	0.1421	0.000224

pCO_2 (atm) = 3.262E-04 - (9.8297E-09)*(elevation in feet)

pO_2 (atm) = 0.20704 - (6.239E-06)*(elevation in feet)

9.5 **Create MINTEQA2 data file using PRODEFA2:** Use the following procedure to create a data file:

1. Start the PRODEFA2 program:

C:\minteqa2\> **prodefa2 [Enter]**

This command runs the PRODEFA2.EXE file. The PRODEFA2 banner screen appears. At the bottom of the screen, the following question will appear:

ENTER FILENAME (enter "X" to exit PRODEFA2) > **filename.dat [Enter]**

*Enter the name you want to call the data file. The screen clears, and PRODEFA2 asks if you want to enter the name of another "seed" file to copy basic information into the file you are now creating. This will shorten data entry if you have similar sample data. TIP: be careful to not enter the seed file name at the previous prompt. Name your data files in a logical manner, be sure to include the ***.dat** extension (signifying DATA), and write down the file name in a notebook that won't get misplaced or lost.*

ENTER filename, R, or press ENTER > **[Enter]**

Now let's create a file from scratch, so don't enter a seed file name, just press [Enter].

2. Begin EDIT LEVEL I data entry:

The EDIT LEVEL I screen should now appear. From here on out, pay attention to the numbers on the left. You will enter the

number of the item you want to change, and then either a question will appear, or you will be given entry instruction:

ENTER CHOICE > **1 [Enter]**

This selects the "Title 1" entry item. Screen clears and the following question appears:

```
Enter problem title (1 of 2 lines)
    OR press ENTER to omit title,
    OR enter "R" to return to previous prompt:
```

California Gulch 1995 Data [Enter]

You will now return to the EDIT LEVEL I screen and continue data entry.

ENTER CHOICE > **2 [Enter]**

Selects the "Title 2" field for entry as above.

```
Enter problem title (2 of 2 lines)
    OR press ENTER to omit title,
    OR enter "R" to return to previous prompt:
```

Stray Horse Gulch SHG01-01-051095 [Enter]

Returns to EDIT LEVEL I screen.

ENTER CHOICE > **3 [Enter]**

Selects the "Temperature (Celsius)" input field. Screen clears.

Enter the temperature between 0 and 100 degrees C. > **5.0 [Enter]**

Returns to EDIT LEVEL I screen.

ENTER CHOICE > **4 [Enter]**

Selects the "Units of Concentration" selection. Screen clears.

```
Select units for concentration . . .(more info, deleted here)
  1 = molal
  2 = mg/L
  3 = ppm
  4 = meq/L
    ENTER CHOICE ([D] = 1) >  2 [Enter]
```

Select 2 for mg/L, milligrams per liter, the usual selection for chemical data.

For conversion from molality to any other unit . . . *(more info, deleted here)*

Do you want to proceed with the conversion ? (Y,N, [D]=Y) > **Y [Enter]**

Returns to EDIT LEVEL I screen.

ENTER CHOICE > **12 [Enter]**

Selects "The pH is: FIXED at" entry field. Screen clears and the following appears:

```
Select pH option:
  1 = Specify EQUILIBRIUM pH
  2 = Allow pH to be computed but specify total hydrogen concentration
  R = Return to previous menu

      ENTER CHOICE ([D] = R) > 1 [Enter]
```

Select 1, "Specify EQUILIBRIUM pH" - the usual choice if you have a measured pH value. Use the field measured value if available.

Enter the EQUILIBRIUM pH > **7.56 [Enter]**

Returns to EDIT LEVEL I screen. This completes the usual Level I variables that require input. Leave the output option at INTERMEDIATE and do not change any other options. Pressing [Enter] will now take you to the MAIN MENU Screen.

ENTER CHOICE > **[Enter]**

MAIN MENU screen appears. You now want to select EDIT LEVEL II to enter chemical concentration data.

ENTER CHOICE > **2 [Enter]**

EDIT LEVEL II screen appears.

3. Begin LEVEL II COMPONENT data entry: *This is where the bulk of your chemical data are entered. At the EDIT LEVEL II menu, enter:*

ENTER CHOICE ([D] = R) > **1 [Enter]**

Select option 1, "Specify AQUEOUS COMPONENTS: TOTAL CONCENTRATION OR FIXED ACTIVITIES." Screen clears.

Specify components for which you know the:
1 = TOTAL DISSOLVED CONCENTRATION
2 = FIXED EQUILIBRIUM ACTIVITY
R = Return to the previous options menu (EDIT LEVEL II)
ENTER CHOICE ([D] = R) > **1 [Enter]**

Select "TOTAL DISSOLVED CONCENTRATION." You may now specify components using the first letter of the chemical symbol for the component, let's use calcium, Ca+2, as an example:

- Enter the FIRST LETTER for the COMPONENT:
To identify . . . (additional text deleted here)
OR press ENTER to terminate component entry.
ENTER your choice > **C [Enter]**

PRODEFA2 will now display all valid input components beginning with "C".

1 CO3-2	2 CN-	3 Ca+2	4 Cd+2	5 Cl-
6 Cr+2	7 Cr(OH)2+	8 CrO4-2	9 Cu+1	10 Cu+2
11 Citrate				

Select the number of the appropriate component (0 = NONE) > **3 [Enter]**

Select 3 for Ca+2. PRODEFA2 will now ask for you to enter the mg/L concentration for calcium:

Enter the TOTAL DISSOLVED CONCENTRATION (MG/L) of COMPONENT:
Ca+2 Id # 150 > **23.7 [Enter]**

PRODEFA2 will now repeat the prompt asking for the first letter of the next component you want to enter. Go through you data and select the

appropriate letter for each of your components. When you have entered all concentrations, enter the following:

- Enter the FIRST LETTER for the COMPONENT:
  To identify . . . (additional text deleted here)
OR press ENTER to terminate component entry.
ENTER your choice > **[Enter]**

The following prompt will now appear:

Specify components for which you know the:
1 = TOTAL DISSOLVED CONCENTRATION
2 = FIXED EQUILIBRIUM ACTIVITY
R = Return to the previous options menu (EDIT LEVEL II)
ENTER CHOICE ([D] = R) > **R [Enter]**

REMEMBER: Level II data entry has some input peculiarities that require you to pre-calculate some component data - see section 9.4 above for input conventions and correction factors.

4. Begin LEVEL II entry for GASES at FIXED PARTIAL PRESSURES: Now you are ready to input data regarding atmospheric gases. All surface waters are exposed to atmospheric gases, so these components will affect the resulting equilibrium chemistry. We are still at the EDIT LEVEL II screen:

ENTER CHOICE ([D] = R) > **4 [Enter]**

Selects option 4, "Specify GASES at FIXED partial pressures" screen.

_____ DEFINE GASEOUS SPECIES _____

---- CHOOSE FROM THE FOLLOWING GASES: ----

1-CH4 (g) 2-CO2 (g) 3-O2 (g) 4-Hg (g)
(other gas selections omitted here)

Enter the number corresponding to the gas you want. Enter zero to abort the selection of a gas.

ENTER CHOICE > **2 [Enter]**

Selects CO2 gas. Some thermodynamic data will be displayed for CO2. If you haven't entered carbonate, the PRODEFA2 will advise you that CO3-2 has been added as a component at a total concentration of zero. Press [Enter] at prompt to continue.

Enter the non-zero partial pressure (atm) of CO2 (g) > **0.000224 [Enter]**

This is the partial pressure for CO2 gas at elevation 10,400 feet (Leadville CO). Make sure you check the value before entering, because PRODEFA2 will not display this value later in EDIT LEVEL III.

Corrected log K is 21.810

Do you want to CHANGE the log K value from 21.8098 ? (Y,N) > **N [Enter]**

DO NOT CHANGE the adjusted log K. PRODEFA2 will return to the EDIT LEVEL II screen. Repeat the steps

you did for CO2 and input the O2 partial pressure by selecting option 4 again:

ENTER CHOICE ([D] = R) > **4 [Enter]**

Selects option 4, "Specify GASES at FIXED partial pressures" screen.

_____ DEFINE GASEOUS SPECIES _____

---- CHOOSE FROM THE FOLLOWING GASES: ----

1-CH4 (g) 2-CO2 (g) 3-O2 (g) 4-Hg (g)
(other gas selections omitted here)

Enter the number corresponding to the gas you want. Enter zero to abort the selection of a gas.

ENTER CHOICE > **3 [Enter]**

Selects O2 gas. Some thermodynamic data will be displayed for O2. PRODEFA2 will advise you that E-1 (the electron) has been added as a component at a total concentration of zero. Press [Enter] at prompt to continue.

Enter the non-zero partial pressure (atm) of O2 (g) > **0.1421 [Enter]**

This is the partial pressure for O2 gas at elevation 10,400 feet (Leadville CO). Make sure you check the value before entering, because PRODEFA2 will not display this value later in EDIT LEVEL III.

Corrected log K is -82.273

Do you want to CHANGE the log K value from -82.273 ? (Y,N) > **N [Enter]**

DO NOT CHANGE the adjusted log K. PRODEFA2 will return to the EDIT LEVEL II screen. You have now specified all the gases, and are ready to check your component entry values in EDIT LEVEL III:

ENTER CHOICE ([D] = R) > **R [Enter]**

Returns to MAIN MENU screen.

5. Check and edit data in EDIT LEVEL III: You are now ready to check and correct your component data entry.

ENTER CHOICE > **3 [Enter]**

Displays EDIT LEVEL III Screen and lists COMPONENT data you have entered in a table. Each entry is numbered on the left and the component and concentration is displayed in columns 3 and 4 in the data table. Let's say entry #1 is wrong:

_____ EDIT LEVEL III _____PROB # 1_
_____ Verify or change listing of COMPONENTS _____

Entry	I.D.	Name	Total Conc.	Log Act.(GUESS)	Improve ?
1	150	Ca+2	6.00000E-00	-3.82	YES

```
(other data omitted here...)


Enter Entry # to change or delete (press ENTER to accept all entries) > 1
[Enter]
                                          This lets you edit entry # 1.  Data
                                          table screen clears.  On the edit
                                          screen, the entry with the wrong
                                          concentration is displayed in the
                                          table at the top of the screen:

Entry   I.D.    Name        Total Conc.     Log Act.(GUESS) Improve ?
  1     150     Ca+2        6.00000E-00          -3.82            YES

Select:
 -1 = Delete this component
  1 = Change ID number
  2 = Change name
  3 = Change total concentration
  4 = Change log activity guess
  5 = Allow MINTEQA2 to improve the guess BEFORE iterating

     Enter choice (press ENTER to accept all values and return): > 3 [Enter]

                                          Select option 3 to change
                                          concentration.

Enter the TOTAL dissolved concentration for this component > 65.2 [Enter]

                                          Screen clears and re-displays edit
                                          info with changed value.

Entry   I.D.    Name        Total Conc.     Log Act.(GUESS) Improve ?
  1     150     Ca+2        6.52000E+01                  -3.82            YES

Select:
 -1 = Delete this component
  1 = Change ID number
  2 = Change name
  3 = Change total concentration
  4 = Change log activity guess
  5 = Allow MINTEQA2 to improve the guess BEFORE iterating
     Enter choice (press ENTER to accept all values and return): > [Enter]

                                          Select [Enter] to accept changes.
                                          You will return to the EDIT LEVEL
                                          III screen for COMPONENTS. Repeat
                                          the above process to edit other
                                          values.  When all are correct, press
                                          [Enter] to accept all component
                                          data.  PRODEFA2 will now display a
                                          similar data table for FIXED
                                          SPECIES:

            _______________ EDIT LEVEL III _______________PROB # 1_
          ________ Verify or change listing of FIXED SPECIES ________
Entry   I.D.      Name          Log K         Enthalpy
  1   3301403   CO2 (g)           2.18098E+01   -5.30000E-01
  2   3300021   O2 (g)           -8.22726E+01    1.33830E+02
  3       330   H+1           7.50000E+00     0.00000E-01


Enter Entry # to change or delete (press ENTER to accept all entries) >
[Enter]
```

This accepts all entries, which is the recommended approach since the edit function won't let you enter a new partial pressure. If you have to edit a gas partial pressure, select -1 to delete, go back to EDIT LEVEL II, and re-enter the gas using selection 4.

```
            _______________ EDIT LEVEL III _______________PROB # 1_
        ________ Verify or change listing of EXCLUDED SPECIES ________

Entry   I.D.      Name
  1        1       E-1


Enter Entry # to change or delete (press ENTER to accept all entries) >
[Enter]
```

This accepts all entries, and returns you to the MAIN MENU.

```
            _______________ MAIN MENU: SELECT OPTION_________PROB #1_
(other material omitted here...)

M = multi-problem generator

X = exit (Write the current problem to the new MINTEQA2 input file
    and exit program

   ENTER CHOICE > X [Enter]
```

This exits PRODEFA2 and saves the MINTEQA2 data file to disk. If you want to add problems to this file, select M and edit the file in EDIT LEVEL I and III as above. You are now ready to submit the file and run the MINTEQA2 model:

10. ***Running the MINTEQA2 Model:*** You have now completed the toughest part, and are ready to submit your data file to the MINTEQA2 model for analysis. This easily done by invoking the MINRUN.BAT batch file:

```
C:\MINTEQA2\> minrun [Enter]
```

10.1 This batch file will present a screen that asks for your input data file name. Type the input data file name and press [Enter]. The screen will refresh and will then ask for the name of your output file. Type the output data file name and press [Enter].

10.1.1 Remember to use the same name for the output file as the data file, except for the 3-character extension, *.out. If the screen acts weird, then you haven't added the ANSI.SYS driver to your CONFIG.SYS (or you haven't re-booted since you edited the file).

10.2 As the model runs, you will get a status box telling you the problem and iteration numbers. If the model runs OK, you will get a message to that effect. If the

model does not run, you have not specified the problem correctly, and a red-screen error message will appear.

10.3 Assuming the model ran correctly, you can now edit or print the output file using any word processor able to read simple ASCII text files. A quick way to check the output is to use the Notepad program in Windows.

11. ***Editing the MINTEQA2 output Files:*** Output ASCII text files may be edited with the Notepad or Wordpad Windows word processing programs. Refer to your word processor manual for instructions on how to import and edit ASCII files. Save the edited file as a simple ASCII or RTF (rich text format) file, while the word processor may save the file as ASCII or as a document file. If you use a word processor, be sure to select a 10-point FIXED FONT, such as courier, or line printer and select landscape page orientation. This will make the MINTEQ data tables and output line up correctly on the page.

Why would you want to edit your MINTEQA2 output files? Two reasons: First, you need to quickly *scan* the file to make sure there are no error messages and that MINTEQ ran successfully. Second, because the output files may be huge, you may need to delete unneeded text and data from the file, or create subfiles that may be transferred into spreadsheets or statistics software, or simply used more conveniently for manual data transfer to analysis or plotting software.

Here's the general structure of the output file, and some tips on what to look for, what to delete, and how to export the data:

11.1 **Part 1 of OUTPUT FILE**: (Input Data) This is the general header that summarizes the data from your input file and the initial activity guesses assigned to the input data. It also includes a summation of component cations and anions and an *unspeciated* (calculated based on measured component concentrations) charge balance percentage calculations. Most waters are cation/anion charge balanced, so this is a general check of how good or complete your data set is. High charge balances may suggest poor quality test results, or that an important component, such as nitrate or another trace element, was not entered. Unless the charge balance is within " 10-15% of zero, the model may bomb.

11.2 **Part 2 of OUTPUT FILE**: (Iteration Summary/Error Messages) If you selected INTERMEDIATE output option in PRODEFA2, Part 2 will not print out. Part 2 summarizes the iteration log of what happened computationally while the model ran. MINTEQ repeats calculations for the input data set several times (minimum of 4-10 times), with each iteration refining species activity guesses until an output solution converges. If the problem does not converge, it has bombed, and the model will print error codes suggesting why, (even if you selected INTERMEDIATE output). If the model ran successfully, then this information may be deleted from the output file.

11.3 **Part 3 of OUTPUT FILE**: (Speciation Tables) This is the heart of the model output. The following tables should appear:

11.3.1 PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE. This is another iteration summary that tells you which components were violating the mass balance restriction imposed by the model at each iteration; another potential marker of problem data if the model bombs. It may be ignored if the model ran OK. Immediately below this table is a table listing entered components, their measured concentration you entered (ANAL MOL for analytical molality, calculated on the input concentrations in mg/L), followed by the final solution molality for the entered components calculated by MINTEQ (CALC MOL). CALC MOL will also appear in the following Part 3 output tables.

11.3.2 Type I - COMPONENTS AS SPECIES IN SOLUTION: Here's the beef. This table starts after a dashed line divider, and it lists the final equilibrium molalities and activities for the components calculated by MINTEQ. Ignore all but the first 5 columns. CALC MOL lists the final calculated molality (moles/1000g H2O - or moles/liter for lower TDS waters) for each component entered followed by ACTIVITY (moles/1000g H2O), the equilibrium activity calculated using the Davies equation. LOG ACTVTY is the base-10 logarithm of the activity, which may be useful in plotting the very low concentration species data.

> Note that the calculated molalities are almost always *less* than the measured concentrations for the entered components, and the activities are always *less* than the calculated molalities.

11.3.3 Type II - OTHER SPECIES IN SOLUTION OR ADSORBED: This table will list all the species molalities and activities that form based on all the components you entered into the problem. The headings are the same as the Type I table. Note that species ID numbers are formed from the ID numbers of the components involved in the reaction. MINTEQA2 groups the species by component, so you can see all the species that formed with iron, for example, at a glance.

11.3.4 Type III and Type IV species may be ignored for simple water chemistry speciation runs.

11.4 **Part 4 of OUTPUT FILE**: (Component Mass Distribution) This section lists the major species for each entered component and provides a convenient percentage breakdown. Use this listing to quickly assess the primary species for the water chemistry you have entered. Species percentages less than 1% are omitted.

11.5 **Part 5 of OUTPUT FILE**: (Equilibrated Mass Distribution) After MINTEQ has solved the problem (the mathematical version of allowing your water sample to reach chemical equilibrium), it will list the final molal concentrations for each component, and provide a final *speciated* charge balance summary along with the calculated ionic strength, the pH (same as you entered) and pe/Eh (redox potential, calculated based on the partial pressure of oxygen).

11.6 **Part 6 of OUTPUT FILE**: (Mineral Saturation Indices) MINTEQA2 assumes that any mineral containing the components you entered may have contributed to the final chemistry. It will calculate a ***saturation index***, a logarithmic value that compares equilibrium solution activities to the equilibrium constant for dissolution of the mineral. *Positive* values suggest that the water is *oversaturated*, and *negative* values suggest *undersaturation* with respect to the specific mineral. An undersaturated mineral will tend to dissolve in the water, while an oversaturated mineral will tend to precipitate out of solution.

> A complete set of water chemistry data will produce a very large list of possible minerals. To simplify this situation, delete or ignore any mineral you know is not present in your system, and any mineral with saturation index > " 2 units. Saturation indices for minerals greater than " 2 suggest that the particular mineral is not affecting the equilibrium solution.

12. Example MINTEQA2 input file created in PRODEFA2:

```
k5345-1.  DH91-5 07/19/99

10.00 MG/L   0.000  0.00000E-01
0 0 1 0 2 0 0 0 1 1 0 0 0
0   0   0
    330  0.000E-01   -6.61 y                    /H+1
    140  2.788E+01   -2.76 y                    /CO3-2
      1  0.000E-01  -16.00 y                    /E-1
    150  1.570E+01   -3.58 y                    /Ca+2
    460  1.770E+00   -3.88 y                    /Mg+2
    500  2.320E+00   -2.84 y                    /Na+1
    410  1.000E+00   -3.04 y                    /K+1
    732  9.650E+00   -3.55 y                    /SO4-2
    180  2.900E+00   -3.17 y                    /Cl-1
    281  4.070E-02   -5.63 y                    /Fe+3
    470  1.000E-06   -6.96 y                    /Mn+2
     30  9.080E-02   -5.35 y                    /Al+3
    770  7.089E+00   -4.03 y                    /H4SiO4

  3   3
3300021   -81.3605   133.8300                  /O2 (g)
3301403    22.7222    -0.5300                  /CO2 (g)
    330     6.6000     0.0000                  /H+1
  6   1
      1     0.0000     0.0000                  /E-1
```

13. Example MINTEQA2 output file (edited for this Appendix).

```
_____________________________________________________________________________
_____________________________ PART 1 of OUTPUT FILE ____________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 17-SEP-99  TIME: 12:23:11


k5345-1.  DH91-5 07/19/99

-------------------------------------------------------------------------------
 Temperature (Celsius):  10.00
 Units of concentration: MG/L
 Ionic strength to be computed.
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed only for those solids specified as ALLOWED
   in the input file (if any).
 The maximum number of iterations is: 100
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file

------------------------------------------------------------------------------
    330  0.000E-01   -6.61 y
    140  2.788E+01   -2.76 y
      1  0.000E-01  -16.00 y
    150  1.570E+01   -3.58 y
    460  1.770E+00   -3.88 y
    500  2.320E+00   -2.84 y
    410  1.000E+00   -3.04 y
    732  9.650E+00   -3.55 y
    180  2.900E+00   -3.17 y
    281  4.070E-02   -5.63 y
    470  1.000E-06   -6.96 y
     30  9.080E-02   -5.35 y
    770  7.089E+00   -4.03 y

 H2O has been inserted as a COMPONENT
  3   3
3300021   -81.3605   133.8300
3301403    22.7222    -0.5300
    330     6.6000     0.0000
  6   1
      1     0.0000     0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS

   ID        NAME       ACTIVITY GUESS    LOG GUESS   ANAL TOTAL
    330  H+1                 2.455E-07        -6.610   0.000E-01
    140  CO3-2               1.738E-03        -2.760   2.788E+01
      1  E-1                 1.000E-16       -16.000   0.000E-01
    150  Ca+2                2.630E-04        -3.580   1.570E+01
    460  Mg+2                1.318E-04        -3.880   1.770E+00
    500  Na+1                1.445E-03        -2.840   2.320E+00
    410  K+1                 9.120E-04        -3.040   1.000E+00
    732  SO4-2               2.818E-04        -3.550   9.650E+00
    180  Cl-1                6.761E-04        -3.170   2.900E+00
    281  Fe+3                2.344E-06        -5.630   4.070E-02
    470  Mn+2                1.096E-07        -6.960   1.000E-06
     30  Al+3                4.467E-06        -5.350   9.080E-02
    770  H4SiO4              9.333E-05        -4.030   7.089E+00
      2  H2O                 1.000E+00         0.000   0.000E-01


     Charge Balance: UNSPECIATED

       Sum of CATIONS=  1.068E-03 Sum of ANIONS =  1.212E-03

       PERCENT DIFFERENCE =  6.320E+00  (ANIONS - CATIONS)/(ANIONS + CATIONS)
```

```
 ----------------------------------------------------
|  IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION: |
|       CO3-2       Log activity guess:    -9.54       |
|       SO4-2       Log activity guess:    -4.00       |
|       Fe+3        Log activity guess:   -13.69       |
|       Mn+2        Log activity guess:   -10.74       |
|       Al+3        Log activity guess:    -9.36       |
|       H4SiO4      Log activity guess:    -4.13       |
|                                                      |
 ----------------------------------------------------
```

PART 3 of OUTPUT FILE

PC MINTEQA2 v3.10 DATE OF CALCULATIONS: 17-SEP-99 TIME: 12:23:11

PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVTY	RESIDUAL
0	Cl-1	8.180E-05	5.943E-04	-3.17000	5.942E-04
1	SO4-2	1.005E-04	-1.185E-08	-4.03174	1.806E-09
2	Fe+3	7.288E-07	2.714E-08	-13.68810	2.707E-08
3	Fe+3	7.288E-07	8.325E-11	-13.70399	1.036E-11

ID	NAME	ANAL MOL	CALC MOL	LOG ACTVTY	GAMMA	DIFF FXN
770	H4SiO4	7.376E-05	7.374E-05	-4.13215	1.000279	7.615E-12
470	Mn+2	1.820E-11	1.801E-11	-10.81110	0.857852	-4.950E-16
30	Al+3	3.365E-06	6.184E-10	-9.35854	0.708236	-4.038E-12
150	Ca+2	3.917E-04	3.869E-04	-3.47898	0.857852	-1.063E-08
460	Mg+2	7.281E-05	7.202E-05	-4.20915	0.857852	-1.979E-09
500	Na+1	1.009E-04	1.009E-04	-4.01283	0.962395	-6.938E-10
410	K+1	2.558E-05	2.556E-05	-4.60901	0.962395	-1.758E-10
732	SO4-2	1.005E-04	9.480E-05	-4.08977	0.857852	-2.600E-09
180	Cl-1	8.180E-05	8.180E-05	-4.10388	0.962395	-5.624E-10
281	Fe+3	7.288E-07	2.791E-14	-13.70404	0.708236	-4.797E-12
140	CO3-2	4.646E-04	3.340E-10	-9.54279	0.857852	0.000E-01
1	E-1	0.000E-01	9.136E-16	-15.03925	0.962395	0.000E-01
330	H+1	0.000E-01	2.610E-07	-6.60000	0.962395	0.000E-01
2	H2O	0.000E-01	4.502E-04	-0.00001	1.000000	0.000E-01

Type I - COMPONENTS AS SPECIES IN SOLUTION

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK
330	H+1	2.610E-07	2.512E-07	-6.60000	0.96239	0.017
140	CO3-2	3.340E-10	2.866E-10	-9.54279	0.85785	0.067
770	H4SiO4	7.374E-05	7.376E-05	-4.13215	1.00028	0.000
150	Ca+2	3.869E-04	3.319E-04	-3.47898	0.85785	0.067
460	Mg+2	7.202E-05	6.178E-05	-4.20915	0.85785	0.067
500	Na+1	1.009E-04	9.709E-05	-4.01283	0.96239	0.017
410	K+1	2.556E-05	2.460E-05	-4.60901	0.96239	0.017
732	SO4-2	9.480E-05	8.133E-05	-4.08977	0.85785	0.067
180	Cl-1	8.180E-05	7.873E-05	-4.10388	0.96239	0.017
281	Fe+3	2.791E-14	1.977E-14	-13.70404	0.70824	0.150
470	Mn+2	1.801E-11	1.545E-11	-10.81110	0.85785	0.067
30	Al+3	6.184E-10	4.380E-10	-9.35854	0.70824	0.150

Type II - OTHER SPECIES IN SOLUTION OR ADSORBED

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK
3301400	HCO3 -	2.303E-06	2.216E-06	-5.65441	0.96239	10.505
3301401	H2CO3 AQ	1.060E-06	1.060E-06	-5.97454	1.00028	16.768
3307320	HSO4 -	1.374E-09	1.322E-09	-8.87882	0.96239	1.828
3300020	OH-	1.260E-08	1.213E-08	-7.91618	0.96239	-14.500
3307700	H3SiO4 -	1.570E-08	1.511E-08	-7.82087	0.96239	-10.272
3307701	H2SiO4 -2	2.049E-14	1.758E-14	-13.75497	0.85785	-22.756
4603300	MgOH +	1.067E-10	1.027E-10	-9.98850	0.96239	-12.363
4601400	MgCO3 AQ	1.342E-11	1.342E-11	-10.87227	1.00028	2.880

```
4601401  MgHCO3 +       1.528E-09  1.470E-09    -8.83256   0.96239     11.536
4607320  MgSO4 AQ       7.882E-07  7.884E-07    -6.10324   1.00028      2.196
1503300  CaOH +         9.447E-11  9.091E-11   -10.04137   0.96239    -13.146
1501400  CaHCO3 +       5.004E-09  4.815E-09    -8.31736   0.96239     11.321
1501401  CaCO3 AQ       1.045E-10  1.045E-10    -9.98078   1.00028      3.041
1507320  CaSO4 AQ       4.820E-06  4.821E-06    -5.31683   1.00028      2.252
5001400  NaCO3 -        2.416E-13  2.325E-13   -12.63362   0.96239      0.939
5001401  NaHCO3 AQ      8.400E-11  8.402E-11   -10.07562   1.00028     10.080
5007320  NaSO4 -        3.720E-08  3.580E-08    -7.44608   0.96239      0.673
4107320  KSO4 -         1.109E-08  1.067E-08    -7.97164   0.96239      0.744
 303300  AlOH +2        7.178E-09  6.158E-09    -8.21058   0.85785     -5.385
 303301  Al(OH)2 +      5.729E-07  5.514E-07    -6.25856   0.96239    -10.083
 303302  Al(OH)4 -      2.225E-08  2.141E-08    -7.66938   0.96239    -24.694
 307320  AlSO4 +        3.198E-11  3.078E-11   -10.51179   0.96239      2.953
 307321  Al(SO4)2 -     1.942E-13  1.869E-13   -12.72835   0.96239      4.826
 303303  Al(OH)3 AQ     2.763E-06  2.763E-06    -5.55857   1.00028    -16.000
2813300  FeOH +2        2.338E-10  2.005E-10    -9.69783   0.85785     -2.527
2817320  FeSO4 +        9.795E-15  9.427E-15   -14.02562   0.96239      3.785
2811800  FeCl +2        3.321E-17  2.849E-17   -16.54535   0.85785      1.329
2811801  FeCl2 +        1.717E-20  1.653E-20   -19.78179   0.96239      2.147
2811802  FeCl3 AQ       1.301E-25  1.301E-25   -24.88566   1.00028      1.130
2813301  FeOH2 +        6.960E-07  6.698E-07    -6.17405   0.96239     -5.653
2813302  FeOH3 AQ       3.132E-08  3.133E-08    -7.50406   1.00028    -13.600
2813303  FeOH4 -        1.296E-09  1.247E-09    -8.90407   0.96239    -21.583
2817321  Fe(SO4)2 -     2.368E-17  2.279E-17   -16.64218   0.96239      5.258
2813304  Fe2(OH)2+4     3.838E-18  2.078E-18   -17.68228   0.54156     -3.208
2813305  Fe3(OH)4+5     7.060E-22  2.708E-22   -21.56740   0.38356     -6.439
4701800  MnCl +         5.113E-15  4.921E-15   -14.30798   0.96239      0.624
4701801  MnCl2 AQ       1.052E-19  1.052E-19   -18.97785   1.00028      0.041
4701802  MnCl3 -        3.881E-24  3.735E-24   -23.42773   0.96239     -0.288
4703300  MnOH +         4.534E-16  4.363E-16   -15.36021   0.96239    -11.132
4703301  Mn(OH)3 -1     1.605E-26  1.545E-26   -25.81113   0.96239    -34.783
4700020  MnO4 -         3.310E-18  3.185E-18   -17.49686   0.96239   -134.665
4700021  MnO4 -2        8.858E-23  7.599E-23   -22.11926   0.85785   -124.199
4707320  MnSO4 AQ       1.883E-13  1.883E-13   -12.72513   1.00028      2.176
4701400  MnHCO3 +       4.600E-16  4.427E-16   -15.35389   0.96239     11.617

-------------------------------------------------------------------------------

 Type III - SPECIES WITH FIXED ACTIVITY

   ID        NAME       CALC MOL       LOG MOL   NEW LOGK     DH
      2  H2O            4.502E-04      -3.347      0.000      0.000
3301403  CO2 (g)        4.613E-04      -3.336     22.743     -0.530
    330  H+            -9.162E-04      -3.038      6.600      0.000
3300021  O2 (g)        -4.147E-18     -17.382    -86.557    133.830

-------------------------------------------------------------------------------

 Type VI - EXCLUDED SPECIES (not included in mole balance)

   ID        NAME       CALC MOL       LOG MOL   NEW LOGK     DH
      1  E-1            9.136E-16     -15.039      0.000      0.000
3301404  CH4 (g)        0.000E-01    -153.388     42.469    -61.000

_______________________________________________________________________________
_____________________________ PART 4 of OUTPUT FILE ______________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 17-SEP-99  TIME: 12:23:11


                 PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
               TYPE I and TYPE II (dissolved and adsorbed) species


H4SiO4
                100.0     PERCENT BOUND IN SPECIES #    770   H4SiO4


Mn+2
                 98.9     PERCENT BOUND IN SPECIES #    470   Mn+2
```

```
                  1.0     PERCENT BOUND IN SPECIES #4707320   MnSO4 AQ
Al+3
                 17.0     PERCENT BOUND IN SPECIES # 303301   Al(OH)2 +

                 82.1     PERCENT BOUND IN SPECIES # 303303   Al(OH)3 AQ

Ca+2
                 98.8     PERCENT BOUND IN SPECIES #    150   Ca+2

                  1.2     PERCENT BOUND IN SPECIES #1507320   CaSO4 AQ

Mg+2
                 98.9     PERCENT BOUND IN SPECIES #    460   Mg+2

                  1.1     PERCENT BOUND IN SPECIES #4607320   MgSO4 AQ

Na+1
                100.0     PERCENT BOUND IN SPECIES #    500   Na+1

K+1
                100.0     PERCENT BOUND IN SPECIES #    410   K+1

SO4-2
                 94.4     PERCENT BOUND IN SPECIES #    732   SO4-2

                  4.8     PERCENT BOUND IN SPECIES #1507320   CaSO4 AQ

Cl-1
                100.0     PERCENT BOUND IN SPECIES #    180   Cl-1

Fe+3
                 95.5     PERCENT BOUND IN SPECIES #2813301   FeOH2 +

                  4.3     PERCENT BOUND IN SPECIES #2813302   FeOH3 AQ

CO3-2
                 68.3     PERCENT BOUND IN SPECIES #3301400   HCO3 -

                 31.5     PERCENT BOUND IN SPECIES #3301401   H2CO3 AQ

E-1
                100.0     PERCENT BOUND IN SPECIES #4700020   MnO4 -

H+1
                 18.0     PERCENT BOUND IN SPECIES # 303301   Al(OH)2 +

                  1.4     PERCENT BOUND IN SPECIES # 303302   Al(OH)4 -

                130.4     PERCENT BOUND IN SPECIES # 303303   Al(OH)3 AQ

                 21.9     PERCENT BOUND IN SPECIES #2813301   FeOH2 +

                  1.5     PERCENT BOUND IN SPECIES #2813302   FeOH3 AQ

H2O
                 10.4     PERCENT BOUND IN SPECIES # 303301   Al(OH)2 +

                 75.1     PERCENT BOUND IN SPECIES # 303303   Al(OH)3 AQ
```

```
                12.6     PERCENT BOUND IN SPECIES #2813301   FeOH2 +

_____________________________________________________________________________
_____________________________ PART 5 of OUTPUT FILE ______________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 17-SEP-99  TIME: 12:23:11


               ----------------------------------------------------
               ----------- EQUILIBRATED MASS DISTRIBUTION -----------


IDX     NAME            DISSOLVED            SORBED            PRECIPITATED
                      MOL/KG   PERCENT    MOL/KG   PERCENT    MOL/KG   PERCENT

770  H4SiO4         7.376E-05   100.0   0.000E-01     0.0   0.000E-01     0.0
470  Mn+2           1.820E-11   100.0   0.000E-01     0.0   0.000E-01     0.0
 30  Al+3           3.365E-06   100.0   0.000E-01     0.0   0.000E-01     0.0
150  Ca+2           3.917E-04   100.0   0.000E-01     0.0   0.000E-01     0.0
460  Mg+2           7.281E-05   100.0   0.000E-01     0.0   0.000E-01     0.0
500  Na+1           1.009E-04   100.0   0.000E-01     0.0   0.000E-01     0.0
410  K+1            2.558E-05   100.0   0.000E-01     0.0   0.000E-01     0.0
732  SO4-2          1.005E-04   100.0   0.000E-01     0.0   0.000E-01     0.0
180  Cl-1           8.180E-05   100.0   0.000E-01     0.0   0.000E-01     0.0
281  Fe+3           7.288E-07   100.0   0.000E-01     0.0   0.000E-01     0.0
140  CO3-2          3.370E-06   100.0   0.000E-01     0.0   0.000E-01     0.0
  1  E-1           -1.655E-17   100.0   0.000E-01     0.0   0.000E-01     0.0
330  H+1           -6.358E-06   100.0   0.000E-01     0.0   0.000E-01     0.0
  2  H2O            1.103E-05   100.0   0.000E-01     0.0   0.000E-01     0.0


     Charge Balance: SPECIATED

       Sum of CATIONS =  1.046E-03 Sum of ANIONS   2.738E-04

       PERCENT DIFFERENCE =   5.850E+01  (ANIONS - CATIONS)/(ANIONS + CATIONS)

     EQUILIBRIUM IONIC STRENGTH (m) =   1.214E-03

     EQUILIBRIUM pH                 =   6.600

     EQUILIBRIUM pe                 =  15.039   or Eh  =   844.90 mv

     DATE ID NUMBER:          990917
     TIME ID NUMBER:        12231197


_____________________________________________________________________________
_____________________________ PART 6 of OUTPUT FILE ______________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 17-SEP-99  TIME: 12:23:11


Saturation indices and stoichiometry of all minerals

    ID #     NAME      Sat. Index        Stoichiometry in [brackets]
  2003000 ALOH3(A)       -0.989    [  1.000]  30  [  3.000]   2  [ -3.000] 330
  6003000 ALOHSO4        -3.618    [ -1.000] 330  [  1.000]  30  [  1.000] 732
                                   [  1.000]   2
  6003001 AL4(OH)10SO4    1.776    [-10.000] 330  [  4.000]  30  [  1.000] 732
                                   [ 10.000]   2
  6041000 ALUM K        -16.697    [  1.000] 410  [  1.000]  30  [  2.000] 732
                                   [ 12.000]   2
  6041001 ALUNITE         0.234    [  1.000] 410  [  3.000]  30  [  2.000] 732
                                   [  6.000]   2  [ -6.000] 330
  6015000 ANHYDRITE      -3.078    [  1.000] 150  [  1.000] 732
  5015000 ARAGONITE      -4.811    [  1.000] 150  [  1.000] 140
  5046000 ARTINITE      -15.477    [ -2.000] 330  [  2.000] 460  [  1.000] 140
                                   [  5.000]   2
  2003001 BOEHMITE        0.771    [ -3.000] 330  [  1.000]  30  [  2.000]   2
  2046000 BRUCITE        -8.805    [  1.000] 460  [  2.000]   2  [ -2.000] 330
  5015001 CALCITE        -4.615    [  1.000] 150  [  1.000] 140
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2077000 CHALCEDONY     -0.430    [ -2.000]   2  [  1.000] 770
8646000 CHRYSOTILE    -15.518    [ -6.000] 330  [  3.000] 460  [  2.000] 770
                                 [  1.000]   2
8246000 CLINOENSTITE   -7.256    [ -1.000]   2  [  1.000] 460  [  1.000] 770
                                 [ -2.000] 330
2077001 CRISTOBALITE   -0.332    [ -2.000]   2  [  1.000] 770
2003002 DIASPORE        2.612    [ -3.000] 330  [  1.000]  30  [  2.000]   2
8215000 DIOPSIDE      -10.692    [ -2.000]   2  [  1.000] 150  [  1.000] 460
                                 [  2.000] 770  [ -4.000] 330
5015002 DOLOMITE      -10.096    [  1.000] 150  [  1.000] 460  [  2.000] 140
6046000 EPSOMITE       -6.049    [  1.000] 460  [  1.000] 732  [  7.000]   2
8646003 SEPIOLITE(C)  -11.387    [ -0.500]   2  [  2.000] 460  [  3.000] 770
                                 [ -4.000] 330
2028100 FERRIHYDRITE    1.205    [ -3.000] 330  [  1.000] 281  [  3.000]   2
4128100 FEOH)2.7CL.3    5.925    [ -2.700] 330  [  1.000] 281  [  2.700]   2
                                 [  0.300] 180
6028100 FE2(SO4)3     -45.553    [  2.000] 281  [  3.000] 732
8046000 FORSTERITE    -16.332    [ -4.000] 330  [  2.000] 460  [  1.000] 770
2003003 GIBBSITE (C)    0.786    [ -3.000] 330  [  1.000]  30  [  3.000]   2
3003000 Al2O3          -2.097    [  2.000]  30  [  3.000]   2  [ -6.000] 330
2028102 GOETHITE        5.034    [ -3.000] 330  [  1.000] 281  [  2.000]   2
6015001 GYPSUM         -2.711    [  1.000] 150  [  1.000] 732  [  2.000]   2
4150000 HALITE         -9.663    [  1.000] 500  [  1.000] 180
3028100 HEMATITE       15.002    [ -6.000] 330  [  2.000] 281  [  3.000]   2
5015003 HUNTITE       -25.310    [  3.000] 460  [  1.000] 150  [  4.000] 140
5046001 HYDRMAGNESIT  -39.278    [  5.000] 460  [  4.000] 140  [ -2.000] 330
                                 [  6.000]   2
6050000 JAROSITE NA    -3.909    [ -6.000] 330  [  1.000] 500  [  3.000] 281
                                 [  2.000] 732  [  6.000]   2
6041002 JAROSITE K     -0.715    [ -6.000] 330  [  1.000] 410  [  3.000] 281
                                 [  2.000] 732  [  6.000]   2
6028101 JAROSITE H     -6.333    [ -5.000] 330  [  3.000] 281  [  2.000] 732
                                 [  7.000]   2
8450000 MAGADIITE     -12.038    [ -1.000] 330  [ -9.000]   2  [  1.000] 500
                                 [  7.000] 770
3028101 MAGHEMITE       5.806    [ -6.000] 330  [  2.000] 281  [  3.000]   2
5046002 MAGNESITE      -5.962    [  1.000] 460  [  1.000] 140
6050001 MIRABILITE    -10.264    [  2.000] 500  [  1.000] 732  [ 10.000]   2
3050000 NATRON        -15.646    [  2.000] 500  [  1.000] 140  [ 10.000]   2
5046003 NESQUEHONITE   -8.356    [  1.000] 460  [  1.000] 140  [  3.000]   2
8646001 PHLOGOPITE    -42.645    [-10.000] 330  [  1.000] 410  [  3.000] 460
                                 [  1.000]  30  [  3.000] 770
2077002 QUARTZ          0.115    [ -2.000]   2  [  1.000] 770
8646004 SEPIOLITE(A)  -13.195    [ -0.500]   2  [  2.000] 460  [  3.000] 770
                                 [ -4.000] 330
2077003 SIO2(A,GL)     -0.942    [ -2.000]   2  [  1.000] 770
2077004 SIO2(A,PT)     -1.270    [ -2.000]   2  [  1.000] 770
8646002 TALC          -13.970    [ -4.000]   2  [  3.000] 460  [  4.000] 770
                                 [ -6.000] 330
6050002 THENARDITE    -11.959    [  2.000] 500  [  1.000] 732
5050001 THERMONATR    -17.802    [  2.000] 500  [  1.000] 140  [  1.000]   2
8215001 TREMOLITE     -28.958    [ -8.000]   2  [  2.000] 150  [  5.000] 460
                                 [  8.000] 770  [-14.000] 330
3047000 HAUSMANNITE   -14.207    [ -8.000] 330  [ -2.000]   1  [  3.000] 470
                                 [  4.000]   2
2047003 PYROCROITE    -13.576    [ -2.000] 330  [  1.000] 470  [  2.000]   2
5047000 RHODOCHROSIT  -10.025    [  1.000] 470  [  1.000] 140
4147000 MNCL2, 4H2O   -21.054    [  1.000] 470  [  2.000] 180  [  4.000]   2
6047000 MNSO4         -18.171    [  1.000] 470  [  1.000] 732
8450001 ANALCIME       -2.842    [  1.000] 500  [  1.000]  30  [  2.000] 770
                                 [ -1.000]   2  [ -4.000] 330
8603000 HALLOYSITE      2.082    [  2.000]  30  [  2.000] 770  [  1.000]   2
                                 [ -6.000] 330
8603001 KAOLINITE       5.523    [  2.000]  30  [  2.000] 770  [  1.000]   2
                                 [ -6.000] 330
8415000 LEONHARDITE     8.346    [ -1.000]   2  [-16.000] 330  [  2.000] 150
                                 [  8.000] 770  [  4.000]  30
8450002 LOW ALBITE     -2.635    [  1.000] 500  [  1.000]  30  [  3.000] 770
                                 [ -4.000] 330  [ -4.000]   2
8450003 ANALBITE       -3.650    [  1.000] 500  [  1.000]  30  [  3.000] 770
                                 [ -4.000] 330  [ -4.000]   2
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8641000 MUSCOVITE       5.625    [  1.000] 410  [  3.000]  30  [  3.000] 770
                                 [-10.000] 330
8415001 ANORTHITE      -5.834    [  1.000] 150  [  2.000]  30  [  2.000] 770
                                 [ -8.000] 330
8603002 PYROPHYLLITE    5.952    [  2.000]  30  [  4.000] 770  [ -4.000]   2
                                 [ -6.000] 330
8415002 LAUMONTITE     -2.344    [  1.000] 150  [  2.000]  30  [  4.000] 770
                                 [ -8.000] 330
8415003 WAIRAKITE      -7.247    [  1.000] 150  [  2.000]  30  [  4.000] 770
                                 [ -8.000] 330  [ -2.000]   2
2015000 LIME          -24.872    [ -2.000] 330  [  1.000] 150  [  1.000]   2
2015001 PORTLANDITE   -14.146    [ -2.000] 330  [  1.000] 150  [  2.000]   2
2046001 PERICLASE     -13.922    [ -2.000] 330  [  1.000] 460  [  1.000]   2
3046000 SPINEL         -9.919    [ -8.000] 330  [  1.000] 460  [  2.000]  30
                                 [  4.000]   2
3046001 MAG-FERRITE     1.830    [ -8.000] 330  [  1.000] 460  [  2.000] 281
                                 [  4.000]   2
8215002 WOLLASTONITE   -8.164    [ -1.000]   2  [ -2.000] 330  [  1.000] 770
                                 [  1.000] 150
8215003 P-WOLLSTANIT   -9.075    [ -1.000]   2  [ -2.000] 330  [  1.000] 770
                                 [  1.000] 150
8015001 CA-OLIVINE    -24.463    [ -4.000] 330  [  1.000] 770  [  2.000] 150
8015002 LARNITE       -26.054    [ -4.000] 330  [  1.000] 770  [  2.000] 150
8015007 CA3SIO5       -52.965    [ -6.000] 330  [  1.000] 770  [  3.000] 150
                                 [  1.000]   2
8015003 MONTICELLITE  -17.611    [ -4.000] 330  [  1.000] 770  [  1.000] 150
                                 [  1.000] 460
8015005 AKERMINITE    -30.272    [ -1.000]   2  [ -6.000] 330  [  2.000] 770
                                 [  2.000] 150  [  1.000] 460
8015004 MERWINITE     -42.812    [ -8.000] 330  [  2.000] 770  [  1.000] 460
                                 [  3.000] 150
8441000 KALSILITE      -5.661    [ -4.000] 330  [  1.000] 770  [  1.000]  30
                                 [  1.000] 410
8441001 LEUCITE        -3.112    [ -2.000]   2  [ -4.000] 330  [  2.000] 770
                                 [  1.000]  30  [  1.000] 410
8441002 MICROCLINE     -1.058    [ -4.000]   2  [ -4.000] 330  [  3.000] 770
                                 [  1.000]  30  [  1.000] 410
8441003 H SANIDINE     -1.579    [ -4.000]   2  [ -4.000] 330  [  3.000] 770
                                 [  1.000]  30  [  1.000] 410
8450004 NEPHELINE      -6.611    [ -4.000] 330  [  1.000] 770  [  1.000]  30
                                 [  1.000] 500
8015006 GEHLENITE     -25.138    [-10.000] 330  [  2.000]  30  [  1.000] 770
                                 [  2.000] 150  [  3.000]   2
3028102 LEPIDOCROCIT    4.725    [ -3.000] 330  [  1.000] 281  [  2.000]   2
8650000 NA-NONTRONIT   15.830    [ -7.320] 330  [ -2.680]   2  [  0.330]  30
                                 [  2.000] 281  [  0.330] 500  [  3.670] 770
8641002 K-NONTRONITE   16.679    [ -7.320] 330  [ -2.680]   2  [  0.330]  30
                                 [  2.000] 281  [  0.330] 410  [  3.670] 770
8615000 CA-NONTRONIT   22.959    [ -7.320] 330  [ -2.680]   2  [  0.330]  30
                                 [  2.000] 281  [  0.167] 150  [  3.670] 770
8646005 MG-NONTRONIT   22.537    [ -7.320] 330  [ -2.680]   2  [  0.330]  30
                                 [  2.000] 281  [  0.167] 460  [  3.670] 770
8646006 Montmorillon    5.122    [  3.810] 770  [  0.490] 460  [ -6.760] 330
                                 [ -3.240]   2  [  0.220] 281  [  1.710]  30
```

Appendix 3

Example Calculations for Flow-Weighted Mass Wasting and Void Formation from Mineral Dissolution

The following notes cover the precautions and procedures for calculating mass wasting and void formation. This example is from investigations at Horsetooth Dam (Craft and Pearson, 2002).

1. **Net increase in seepage:** For each analyzed constituent, same date reservoir mg/L is subtracted from seepage mg/L to calculate net difference mg/L. Overall net difference was calculated by subtracting reservoir mg/L sum of ions from seepage mg/L sum of ions.

   $mg/L_{seepage} - mg/L_{reservoir} = mg/L_{net}$

   Sum of ions = $(Ca + Mg + Na + K + HCO_3^- + CO_3^{2-} + OH^- + SO_4^{2-} + Cl^- + Al + Fe + Mn + Si)$, mg/L

   Trace elements (Al, Fe, Mn, Si) reported below detection limits were re-coded as one-half the reported limit of detection before net mg/L were calculated.

2. **Simplified geochemical model:** The geology of the Lykins formation is complex and several simplifying assumptions about dissolution reactions were used to calculate seepage mass loadings and dissolution void space formation rates. These assumptions involve the expression of mass loadings and void volumes as gypsum or anhydrite, along with calcite. Other processes also act to increase net ions in seepage, however, these reactions lack the clear supportive evidence that is available for calcite, gypsum, and anhydrite.

   Increases observed in seepage SO_4^{2-} are likely caused by dissolution of both gypsum and anhydrite, but here net SO_4^{2-} was calculated assuming that all increased SO_4^{2-} was caused by only gypsum or only anhydrite. Gypsum (D = 2.30 to 2.37 g/cm^3) is less dense than anhydrite (D = 2.9 to 3.0 g/cm^3), so void volume rate estimates calculated assuming gypsum will be higher than those assuming anhydrite. These two density assumptions provide a range of void formation rates for soluble sulfate minerals.

   The limestones in the Lykins Formation are composed of both calcite and dolomite. Calcite will only produce Ca and CO_3^{2-} (as HCO_3^- below pH 8.3) upon dissolution, while dolomite will produce Ca, Mg, and CO_3^{2-}. The Ca:Mg ratio associated with dolomite deposits along specific flow paths is unknown, so a stoichiometric geochemical model for dolomite dissolution is unavailable. Since dolomite dissolution would be the cause of increased seepage Mg concentrations (along with Ca), net meq/L Mg was added to net meq/L Ca to calculate limestone mass loadings and void space formation rates *as calcite.* While this assumption will produce higher estimates for limestone mass loading, the comparable densities of calcite (2.72 to 2.94 g/cm^3) and dolomite (2.86 to 2.93 g/cm^3), will produce similar dissolution void formation rates. Net meq/L for limestone dissolution was calculated as follows:

   $(Ca_{net\ meq/L} - SO_4^{2-}{}_{net\ meq/L}) + Mg_{net\ meq/L}$

3. **Specific assumptions:**

a. If same date seepage flow and reservoir elevations were unavailable, the closest available date was used.

b. meq/L and mg/L data were averaged for 5/19/00 Reservoir, all SM-3 (average of 3N, 3S, and 3V), and all SM-FD98-3 (from field sample duplicates). July 1999 reservoir sample data was used for July 2001 SM-FD98-3 data.

c. Seepage flow for EXSP-1 and EXSP-2 was not measured and was assumed to be 15 gpm (based on contractor pumping rates at the excavation).

d. Net loadings expressed as a mineral were calculated based on meq/L data, which were converted to mass using the following factors:

Gypsum = $CaSO_4@2H_2O$ = 86.0861 mg/meq
Anhydrite = $CaSO_4$ = 68.0708 mg/meq
Limestone (Calcite) = $CaCO_3$ = 50.0047 mg/meq
Silica = SiO_2 = 60.0843 mg/mmol, Si = 28.0855 mg/mmol

e. Conversion factors for units of flow:

1 cfs = 28.3169 L/s = 2.4466 x 10^6 L/d
1 gpm = 3.7854 L/min = 5,451 L/d
1 m^3 = 1,000 L = 1 x 10^6 cm^3 = 35.315 ft^3

f. The higher reported density values (Deer, et al., 1992) were used to calculate void volume formation rates:

Gypsum = 0.00230 to 0.00237 kg/cm^3
Anhydrite = 0.00294 to 0.00300 kg/cm^3
Calcite = 0.00272 to 0.00294 kg/cm^3
Silica = 0.00262 to 0.00265 kg/cm^3

4. **Mass loading calculation, kg/day:**

(mg/L_{net}) x (seepage flow, ft^3/s) x (86,400 s/day) x (28.3169 L/f^3) x (1.0 x 10^{-6} kg/mg)
or
(mg/L_{net}) x (seepage flow, gal/min) x (1,440 min/day) x (3.7854 L/gal) x (1.0 x 10^{-6} kg/mg)

5. **Void volume formation calculation, m^3/day:**

m^3/day = ((mineral loading, kg/day)/(mineral density, kg/cm^3)) x 0.000001 m^3/cm^3

Precautions using mineral loading and void volume formation data: There are several important issues to consider before using or interpreting mass loading or void formation rate

data. First, it would be inappropriate to extrapolate any observed daily loading or void formation rates to annual or multi-year periods without accounting for the changes in seepage flow observed throughout the year. Seepage flow will vary throughout the year depending on the hydrostatic head at changing reservoir elevations and the flow path properties for a particular seep. Although reservoir elevation and seepage flow do not show a simple linear relationship at Horsetooth Dam, all seeps have responded to varying reservoir elevations with generally lower flows at lower reservoir elevations.

Second, a large proportion of the seepage increase in ions may be from biologically mediated processes (respiration and metabolism) and other unknown mineral weathering reactions. Depending on seepage transit time, bacterial respiration can produce pH changes and some of the increases observed for HCO_3^- and CO_3^{2-} ions in seepage. Well samples with elevated pH > 9 suggest contact with grout cement. Ion exchange on clays in the Lykins formation may also account for some the seepage net Na. Finally, incongruent mineral reactions where one mineral partially dissolves to release some ions and form another mineral, may account for a small portion of the net cations and Si.

Third, calculated seepage loadings need to be compared to the *contact volume* of the foundation or abutment along the seepage flow path (Bartholomew and Murray, 1985). At Horsetooth Dam, most seepage paths and contact volumes are poorly understood, and this issue represents the greatest uncertainty in assessing the engineering consequences of mineral dissolution. For example, seepage contact volume would be greater for SM-3, located almost a mile downstream of the dam, compared to SM-2. Seepage flow paths may change over time, forming new paths, and old paths may collapse. Flow paths though brecciated fracture zones are serpentine and "spread out" from the axis of flow in complex patterns. Seepage suggesting structural concern, such as the left side seeps that started emerging in 1999, usually increase over time for similar hydrostatic gradients.

A reasonable approach at Horsetooth Dam should seriously consider loadings and void volume formation rates calculated for gypsum, anhydrite, and limestone (calcite and dolomite). There is clear geological evidence for these simple congruent dissolution reactions.

1. For each analyzed constituent, subtract reservoir mg/L from seepage mg/L to calculate net difference mg/L. Overall net difference was calculated by subtracting reservoir mg/L sum of ions from seepage mg/L sum of ions.

   $mg/L_{seepage} - mg/L_{reservoir} = mg/L_{net}$

   Sum of ions = $(Ca + Mg + Na + K + HCO_3^- + CO_3^{2-} + OH^- + SO_4^{2-} + Cl^- + Al + Fe + Mn + Si)$,mg/L

   Trace elements (Al, Fe, Mn, Si) reported below detection limits were re-coded as one-half the reported limit of detection.

2. kg/day mass loadings were calculated as follows:

(mg/L_{net}) x (seepage flow, ft^3/s) x (86,400 s/day) x (28.3169 L/f^3) x (1.0×10^{-6} kg/mg)
or
(mg/L_{net}) x (seepage flow, gal/min) x (1,440 min/day) x (3.7854 L/gal) x (1.0×10^{-6} kg/mg)

loading calculation assumptions:

a. Seepage flow and reservoir elevations selected from closest available to sampling date.

b. meq/L and mg/L data were averaged for 5/19/00 Reservoir, all SM-3 (average of 3N, 3S, and 3V), and all SM-FD98-3 (from field sample dups). July 1999 reservoir data was used for July 2001 SM-FD98-3.

c. Seepage flow for EXSP-1 and EXSP-2 was not measured and is assumed to be 15 gpm.

d. Net loadings expressed as a mineral were calculated based on meq/L data, which were converted to mass using the following factors:

Gypsum = $CaSO_4 \bullet 2H_2O$ = 86.0708 mg/meq
Calcite = $CaCO_3$ = 50.0047 mg/meq
Silica = SiO_2 = 60.0843 mg/mmol, Si = 28.0855 mg/mmol

All net sulfate was assumed to originate from dissolution of gypsum. Net calcite was calculated based on combining Ca and Mg and then subtracting sulfate. This was calculated as: $((Ca_{net\ meq/L} - SO_4^{2-}{}_{net\ meq/L}) + Mg_{net\ meq/L})$. Net Si was calculated as SiO_2 using a gravimetric adjustment factor = 2.1393.

e. 1 cfs = 28.3169 L/s = 2.4466×10^6 L/d; 1 gpm = 3.7854 L/min = 5,451 L/d
1 m^3 = 1,000 L = 1×10^6 cm^3

f. Density values: Gypsum = 0.00230 to 0.00237 kg/cm^3
Calcite = 0.00272 to 0.00294 kg/cm^3
Silica = 0.00262 to 0.00265 kg/cm^3 (Deer, et.al, 1992)

g. Void volume formation calculation:

m^3/day = ((mineral loading, kg/day)/(mineral density, kg/cm^3)) x 0.000001 m^3/cm^3

4. Example loading and void volume calculations: SM-4 on 7/20/99

	seepage flow, gpm	***sum of ions mg/L***	***Ca meq/L***	***Mg meq/L***	***SO_4^{2-} meq/L***	***Si mg/L***
SM-4	461.45	144	1.15	0.39	0.36	2.13
Reservoir		59.5	0.41	0.14	0.20	0.880
NET CHANGE		84.8	0.74	0.25	0.16	1.25

Gypsum Loading = $SO_4^{2-}{}_{\text{net meq/L}}$ x 86.0708 mg/meq = mg/L as gypsum
= 0.16 meq/L x 86.0708 mg/meq = ***13.7713 mg/L as gypsum***
kg/day = 13.8 mg/L x 461.5 gpm x 3.7854 L/gal x 1,440 min/day x (1.0×10^{-6} kg/mg)
= ***34.7 kg/day*** lost as gypsum (0.01464 m^3/day of void space)

Calcite Loading = (($Ca_{\text{net meq/L}}$ - $SO_4^{2-}{}_{\text{net meq/L}}$) + $Mg_{\text{net meq/L}}$) x 50.0047 mg/meq
= ((0.74 meq/L - 0.16 meq/L) + 0.25 meq/L) x 50.0047 mg/meq
= 0.83 meq/L x 50.0047 mg/meq = ***41.5039 mg/L as calcite***
kg/day = 41.5 mg/L x 461.5 gpm x 3.7854 L/gal x 1,440 min/day x (1.0×10^{-6} kg/mg)
= ***104 kg/day*** lost as calcite (0.035374 m^3/day of void space)

Silica Loading = $Si_{\text{net mg/L as Si}}$ x (molar weight SiO_2)/(molar weight Si)
= $Si_{\text{net mg/L as Si}}$ x 2.1393
= 1.25 mg/L x 2.1393 = 2.674 mg/L as SiO_2
kg/day = 2.67 mg/L x 461.5 gpm x 3.7854 L/gal x 1,440 min/day x (1.0×10^{-6} kg/mg)
= ***6.71 kg/day*** as silica (0.01464 m^3/day of void space)

Total Loading = $\Sigma ions_{\text{net mg/L}}$ x 461.5 gpm x 3.7854 L/gal x 1,440 min/day x (1.0×10^{-6} kg/mg)
kg/day = 84.8 mg/L x 461.5 gpm x 3.7854 L/gal x 1,440 min/day x (1.0×10^{-6} kg/mg)
= ***213 kg/day*** total loading

Appendix 4

Pictorial Guide to Well Sampling

Summary: This pictorial guide describes how to collect seepage water samples from piezometer and observation wells using standard sampling practices.

1. **Preliminary Activities:**

1.1 Calibration of field instruments is an essential preliminary activity before samples are collected. Here a conductivity meter is being calibrated using certified standards of known concentration. Take time to allow the probe to equilibrate in the calibration solution and samples. Record the calibration information on log sheets or in the project sampling notebook, and don't forget to replace batteries!

1.2 Recording field conditions. Chuck Sullivan checks the general wind speed and air temperature while the portable meters are being calibrated. Record these data on log sheets or in the sampling notebook.

1.3 Calibration of the pH meter. The crew is using fresh pH=4 and pH=7 buffer solutions to calibrate the probe. The electrode for any pH meter should be rinsed with deionized (di) water (wash bottle to the right) before and after measurement of a sample, and stored in a real water sample in-between measurements.

1.4 Before selecting the first well to sample, the crew checks the historical piezometer level data and other well records to see what sampling method will be needed. Is this piezometer well intercepting the correct formation? Will we need to use a pump or bailer? How much water do we need to pump or bail before collecting a sample?

1.5 Here's the opened piezometer cover exposing the well casing to the left. The blue cable passing through the well cap is from the vibrating wire piezometer, which has been carefully removed before sampling. Note the plastic tarp in the background used to keep sampling equipment off the dirt and clean.

1.6 Preparing to measure the current depth to water in the well using a water level meter. This particular instrument, a RocTest model CPR-6, whistles when the sensor touched the water surface.

1.7 Here, the tarp is being used to keep the sampling bailers and the piezometer clean. Use the bailer appropriate to the volume you need collect and the depth of the well, and don't forget to rinse with di water before and after collecting the sample.

2. **Bailing a well** - Use a clean bailer to clear (purge) water and collect samples from a well that does not recharge quickly. You may need to clear the well and then come back later in the day if the well does not refill quickly.

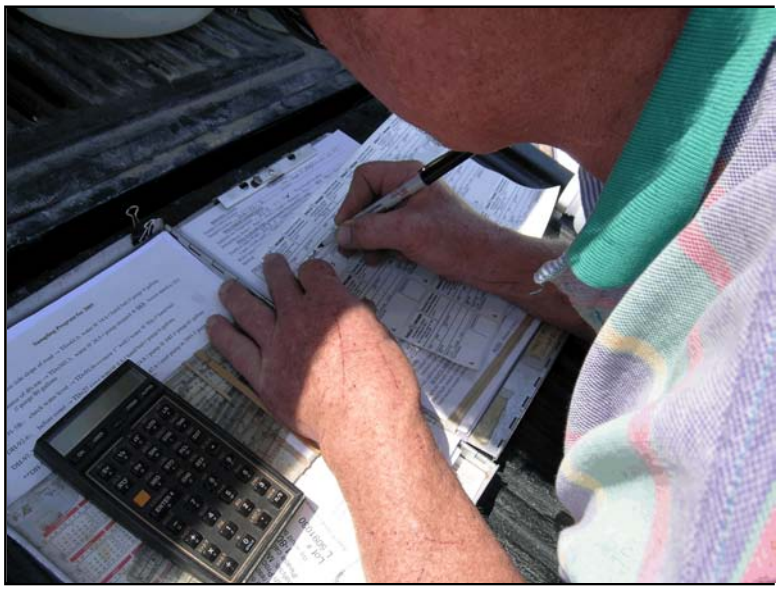
2.1 Did I mention that you should rinse the bailer with deionized water before and after sampling? Inside and outside?

2.2 Lowering the bailer into the well.

2.3 Empty the bailer into a clean plastic bucket. Here we can see that the initial bails are fairly clear. The bucket should have calibration lines so you can estimate the rough volume in the well and record that value on the sampling log sheet or field notebook.

2.4 Use the bucket to measure the EC and pH. Here we can see that the water at the bottom of the well contained sediments. If this is a new site, or the sediment is a new feature for this well, note the observation on the log sheet and collect a separate sample so the solids can be separated (using filtration) and then identified by a petrographer.

2.5 After the well has recharged, collect the fresh sample from the bailer and rinse the sample bottle 3-times with the bailer water before collecting the sample. Dump the rinseate into the bucket. Fill the sample bottle to overflowing and then seal. Shown here is a 500-mL wide-mouth high density polyethylene certified clean bottle.



2.6 Take the time to clearly and neatly fill out the sample labels. Include date, time, station name, sample treatment (raw, filtered, preserved), and the analytical tests requested. Attach the label, put the sample in a zip-loc back, seal, and place in a picnic cooler with ice. Enter any field data and observations in the log sheet or notebook.

3. **Pumping well samples.** Wells that recharge quickly can be sampled with a submersible pump. You should perform the same preliminary activities as for bailing: check the historical data and confirm the well, remove the piezometer, check the water level in the well, place the tarp for keeping samples and equipment clean.

3.1 AC power can be provided by a portable generator. Did you remember to bring extra gas? And when was the last time you did routine maintenance? Aw, what the heck, it'll probably work just fine!

3.2 Here's the submersible Grundfos pump head that is lowered into the well. The hose is attached to a reel (left) that makes lowering and raising the pump more convenient.

3.3 The pump is operated with the controller unit.

3.4 Carefully lower the pump head into the well to the depth of the screen. The hose should be length calibrated with markers.

3.5 Once the correct depth has been reached, a racquet ball or tennis ball can be used to wedge the pump hose so it does not move.

3.6 Start the pump and slowly increase flow. Discharge the effluent into a bucket and dump the contents until the required volume of water has been purged (3-5 well volumes). This particular well required an 85-gal purge volume.

3.7 Once the purge volume has been cleared, place the pump effluent hose in the bucket continue pumping. Monitor the pH, EC, and T of the water as seen here. When the readings are stable, record the data in the log sheet or notebook.

3.8 When the EC and T have stabilized, remove the hose and collect the sample. Rinse the sample bottle 3-times with well water and then fill the bottle to overflowing before sealing. Label as before, put the sample in a zip-loc bag, seal it, and then place the sample in a picnic cooler with ice.

Appendix 5

Glossary of Technical Terms and Conversion Factors

Glossary of Technical Terms

AA: chemistry - atomic absorption, a spectrophotometric instrumental method used to analyze for trace elements

AAS: chemistry - atomic absorption spectrophotometer

absorption: chemistry - the atomic process whereby an atom or molecule absorbs energy at a given wavelength, causing an electron to move to a higher-energy orbital; the opposite of emission; this term should not be confused with adsorption

abutment: engineering - the structural geology supporting the end of a dam

accuracy: statistics/quality assurance - the closeness of a measured value to the true value

acid mine drainage: geology - acidic water associate with mining activities, created when sulfide minerals such as pyrite are exposed to oxygenated water, creating sulfuric acid

acre: measurement unit - English unit for land area, (1 acre = 2,471 ha)

acre-ft: measurement unit - English volume unit for water, 1 acre-ft = 12,335 m^3 = 325,851 gallons

adsorbed: chemistry - analytes chemically bound or otherwise attached to the surface of a particle

adsorption: chemistry - the process whereby a chemical compound attaches to a surface; adsorption may involve several attractive forces, including van der Waal's forces, electrostatic attraction, or chemical bonding; this term should not be confused with absorption

aerobic: biology/chemistry - with oxygen

agglomerates: geology - clumps of loosely consolidated solid materials

albite: geology - a plagioclase feldspar enriched with sodium: $NaAlSi_3O_8$

algae: biology - microscopic aquatic plants that contain chlorophyll

alkalinity: chemistry - the acid neutralizing components in water, usually carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and hydroxide (OH^-); often reported in mg/L as $CaCO_3$

alluvium: geology - unconsolidated gravel, silt and sand deposited in recent geological times by flowing water: alluvial deposit, alluvion

alteration, altered: geology - change in the mineralogical composition of rock by physical or chemical means, usually applied to hydrothermal solution processes

anaerobic: biology/chemistry - without oxygen

analyte: chemistry - the chemical compound or constituent being detected or analyzed

anions: chemistry - negatively charged ions, usually the major anions: HCO_3^-, CO_3^{2-}, SO_4^{2-}, and Cl^-

anorthite: geology - a plagioclase feldspar enriched with calcium: $CaAl_2Si_2O_8$

anoxic: biology - an environment without oxygen; synonym for anaerobic

ANSI: American National Standards Institute

apatite: geology - a group of calcium phosphate-containing minerals, also containing carbonate, fluoride, chloride, or hydroxide

APHA: American Public Health Association

arkose, arkosic: geology - a feldspar-rich sandstone derived from rapid disintegration of granite

ASA: American Society of Agronomy

ASCE: American Society of Civil Engineers

ASQC: American Society for Quality Control

ASTM: American Society for Testing and Materials

atm: chemistry - atmosphere, SI unit, equal to the atmospheric pressure at mean sea level

AWWA: American Water Works Association

basalt: geology - an igneous volcanic rock

benthic: limnology - associated with sediments below the water column, or the bottom of a stream or lake

bias: statistics/quality assurance - a consistent deviation of measured values from the true value caused by a systematic error

biotic: biology - associated with biological organisms

blank: chemistry-QA/QC - a clean check sample used to test for contamination during an instrument run.

blind: chemistry-QA/QC - a check sample or standard submitted to a lab disguised as a normal sample.

breccia: geology - a coarse-grained rock composed of angular broken rock fragments held together with mineral cement

C: chemistry - the element carbon; coulomb, SI unit for electric charge

Ca, Ca^{2+}: chemistry - the element calcium, or calcium ion

calcite: geology - mineral calcium carbonate, $CaCO_3$

calibration verification: chemistry-QA/QC - a known concentration certified standard, different from the standards used to calibrate an instrument, that is analyzed after calibration and during the period the instrument is analyzing samples. Used to independently verify initial (ICV) and continuing calibration (CCV).

Cambrian: geology - rocks formed during the older period of the Paleozoic Era, from 570 to 510 million years ago

carbonates: geology - minerals containing carbonate, such as calcite or dolomite

cations: chemistry - positively charged ions, usually Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}

Celsius, °C: SI metric temperature scale with 0° set to the freezing point of water, and 100° to the boiling point of water at 1 atm pressure; formerly called centigrade

certified: chemistry-QA/QC - as applied to a standard, having documentation attesting to the precision, accuracy, and traceability of a reported concentration.

cfs, ft^3/s: measurement unit - cubic feet per second, English and engineering unit for flow discharge, 100 ft^3/s = 28,317 liters per second

check sample: chemistry-QA/QC - a sample analyzed during an instrument run having known concentrations, not necessarily certified or traceable.

chlorite: geology - a group of clay-like minerals of the general formula: $(Mg, Fe^{2+}, Fe^{3+})_6AlSi_3O_{10}(OH)_8$

chlorophyll: biochemistry - the green pigment in most plants

Cl, Cl^-: chemistry - the element chlorine, or the chloride ion

classification plot: geochemistry - a graph that plots more than 2 variables in order to classify samples based on similar behavior; examples - Piper diagrams, principal components plots

clastic: geology - pertaining to a rock or sediment composed of broken fragments of rocks and minerals transported some distance from their points of origin. Sandstone and shale are considered Aclastics@

clay: geology - a class of finely crystalline or amorphous single and multi-layered aluminosilicate minerals formed from the weathering of feldspars, pyroxenes, and amphiboles; or soil and sediment particles smaller than 0.004 :m containing clay minerals such as illite, smectite, or montmorillonite

CO_2: chemistry - carbon dioxide gas

CO_3^{2-}: chemistry - carbonate, or carbonate ion

colloid: chemistry - very small particles suspended in water that do not settle

colorimetric: chemistry - a spectrophotometric analytical method that uses a chemical to react with the analyte to form a colored compound The intensity of the colored compound is related to concentration

composite sample: sampling/QA - a combined sample containing subsamples collected from different locations, depths, or times, used to represent a larger population

conglomerate: geology - a coarse-grained clastic sedimentary rock composed of granules, pebbles, and cobbles larger than 2mm in diameter (gravel) in a matrix of fine sands and silts

Cretaceous: geology - rocks formed during the final period of the Mesozoic era, covering the span of time from 65 to 135 million years ago

dikes: geology - a vertical igneous intrusion that cuts across the bedding or foliation of the country rock: also sill, dyke; engineering - a short embankment or dam

diorite: geology - a group of plutonic rocks of intermediate acid-base composition containing visible hornblende, acid plagioclase (oligoclase, andesine), pyroxene, and some quartz Also andesite

dip: geology - the maximum angle to the horizontal made by a bedding or fault plane

dissolved: chemistry - an operationally defined term applied to water analysis results, usually meaning that the sample is filtered through a 0.45-:m pore-size membrane filter before analysis

diversion, diversion dam: engineering - a structure that diverts water from a river or other water body; a dam that partially blocks a river or stream to allow diversion of water into canals or other conveyance structures

DL: chemistry-QA/QC - detection limit.

DO: chemistry - dissolved oxygen, mg/L

DOC: chemistry - dissolved organic carbon

dolomite: geology - a carbonate mineral containing both calcium and magnesium: $Ca_aMg_b(CO_3)_{a+b}$

earthen dam; embankment dam: engineering - a dam constructed from compacted soil

EC: chemistry - electrical conductivity, measured in microsiemens per centimeter, :S/cm; also electron capture detector, a detector on a gas chromatograph that is sensitive to halogens in organic compounds

Eh: chemistry - redox or oxidation-reduction potential, measured in millivolts, mV

electrometric: chemistry - analysis using measurement of electrical potential (voltage), as with an electrode that measures pH

electroneutrality: chemistry - a property of natural waters where positive ions

(sum of cations) and negative ions (sum of anions) have equal concentrations (in meq/L); this principle can be used to independently check analysis results for major ions; see ion balance

embankment: engineering - a structure of compacted earth or soil that usually contains or impounds water

Entrada Sandstone: geology - a sedimentary rock formation deposited during the middle Jurassic period, usually observed below the Morrison shale and above the Navajo Sandstone

Eocene: geology - the Eocene Epoch; rocks deposited or formed 55 to 35 million years ago, between the Oligocene (more recent) and the Paleocene (older) strata

eolian, aeolian: geology - wind-blown

EPA, USEPA: US Environmental Protection Agency

epilimnion: limnology - the surface layer of a thermally stratified lake

epithermal: geology - pertaining to hydrothermal mineral deposits formed in the upper 1 km of the earth's surface at temperatures of 50°-200°C

EPRI: Electric Power Research Institute

eq/L: chemistry/measurement unit - equivalents per liter

equilibrium: chemistry - the state in a chemical reaction within a closed system when the forward and reverse reaction rates are equal

equivalent: chemistry/measurement unit - a chemical concentration unit based on reactivity, equal to the molar weight divided by the valence of the compound or ion

eutrophic: limnology - trophic state of a lake having high productivity, generally low water transparency, abundant nutrients for plankton, and elevated concentrations of organic carbon

evaporite: geology - a mineral formed when water evaporates

faculative: biology - referring to bacteria in water capable of respiring both dissolved oxygen under aerobic conditions, and other chemical forms containing oxygen uner anaerobic conditions

fault: geology - a crack or fracture in rock, or a zone of fracturing with displacement of sides parallel to the fracture

fault block: geology - a crustal unit bounded by faults that tectonically behaves as a single unit

Fe: chemistry - the element iron

Fe^{2+}: chemistry - the ferrous ion, a reduced form of iron in the +II oxidation state; the stable form of iron found in anaerobic waters and sediments

Fe^{3+}: chemistry - the ferric ion, an oxidized form of iron in the +III oxidation state; the stable form of iron in oxygenated waters

feldspar: geology - a class of metamorphic aluminosilicate minerals

felsic: geology - pertaining to a group of igneous rocks composed of light colored minerals such as quartz, feldspars, feldspathoids, or muscovite

ferrihydrite : geology - an iron hydroxide mineral: $Fe(OH)_3$

filtrate: chemistry - the liquid passed through a filter

flow: measurement unit - volume per unit time passing a measurement point

flow-weighting: engineering/hydrology - multiplying a concentration times flow to estimate mass wasting or mass transport

flowpath: seepage - the path that seepage follows underneath or around a dam or embankment

fluorescence: chemistry - the emission of light caused by incident light, a spectrophotometric analysis method based on fluorescence

foundation: engineering - the structural geology beneath and supporting a dam

fractional spooning: sampling/QA - a procedure for collecting representative subsamples using many small, randomly selected scoops of solid material

fugitive dust: meteorology - wind-blown dust, fine soil, and sediment transported away from its point of origin

fulvic acid, fulvic materials: chemistry - a heterogeneous and polydisperse class of organic compounds with molecular weights from 600 to 2,000 amu, found in natural soil and water environments, that includes fatty acids, proteins, polysaccharides, and their hydrolysis products Fulvic materials account for most of the DOC in natural waters Like humic materials, fulvic materials are formed by the decomposition of living matter, but are usually more soluble than the higher molecular weight humic materials

functional group: chemistry - a reactive site on a molecule

G: SI unit prefix for giga, or 10^9

g: measurement unit - gram, SI mass unit

gabbro: geology - a group of dark colored intrusive igneous rocks composed of calcium plagioclase and other minerals; a coarse-grained equivalent of basalt

geotechnical: engineering - pertaining to the use of engineered soils in structures

geothermal : geology - pertaining to heat from the interior of the earth

GFAA: chemistry - graphite furnace atomic absorption

glacier, glaciation: geology - a large mass of ice formed mostly on land from the compression and recrystallization of snow, which slowly flows downhill; the process of glacier formation

glass: geology - a non-crystalline rock formed from the rapid cooling of magma

gneiss: geology - a foliated textured rock formed by regional metamorphism

grab sample: chemistry-QA/QC - a randomly selected single sample

granite: geology - a hard plutonic rock, containing mostly quartz and feldspar

granodiorite: geology - a coarse-grained plutonic rock intermediate in composition between quartz diorite and quartz monzonite; a diorite containing quartz and alkali feldspar

H_2S: chemistry - hydrogen sulfide, a gas that smells like rotten eggs, usually associated with stagnant water and prolonged anaerobic conditions

ha: measurement unit - hectare, SI area unit (1 ha = 1.00 X 10^4 m^2)

hardness: chemistry - the sum of divalent ions in a water sample, usually calculated as calcium + magnesium, and often reported in mg/L as $CaCO_3$

HCO_3^-: chemistry - bicarbonate, or bicarbonate ion, the dominant form of alkalinity in most natural surface waters

head: hydrology - hydrostatic potential, or pressure difference between two water surfaces or depths, usually expressed in feet or inches of water

head differential: hydraulic engineering - water pressure difference across the surface of a screen, louver, or other positive barrier structure, usually measured in inches of water

hematite : geology - an iron oxide mineral: "-Fe_2O^3

heterogeneous: chemistry - poorly mixed and having different phases, such as a solid dispersed nonuniformly in a liquid, or as with soil composed of many minerals in a random mixture

histogram: statistics - a graph of ranked and grouped data that shows the distributional properties of the variable; a graph of number of observations within ranked groups (called cells, based on an arbitrary range of data values) vs value

Holocene: geology - an epoch of the Quaternary period, after the Pleistocene, approximately 8,000 years ago to the present

homogeneous: chemistry - completely and uniformly mixed, as with dissolved constituents in water

hornblende: geology - the most common mineral in the amphibole group, having a general formula: $Ca_2Na(Mg, Fe^{2+})_4(Al, Fe^{3+},Ti)$

humic acid, humic materials: chemistry - a heterogeneous and polydisperse class of high average molecular weight (> 2,500 amu) organic compounds found in natural soil and water environments that includes fatty acids, proteins, polysaccharides and their hydrolysis products Humic materials are formed by the decomposition of living matter, and are usually less soluble than the lower molecular weight fulvic materials

hydrated: geology - a mineral or compound containing water

hydrodynamics: limnology - the study of water flows and currents

hydrology: the study of surface and ground water hydrodynamics

hydrothermal: geology - processes in igneous rock involving heated or superheated water

hypolimnion: limnology - the cold and dense water pool in a thermally stratified lake, next to sediments and below the thermocline

IC: chemistry - ion chromatograph

ICP-ES: chemistry - inductively-coupled plasma - emisssion spectrograph

ICP-MS: chemistry - inductively-coupled plasma - mass spectrometer

ICV: chemistry-QA/QC - initial calibration verification, a standard or standard reference material solution of known concentration used to confirm instrument calibration.

IDL: chemistry-QA/QC - instrument detection limit.

IEC: International Electrotechnical Committee

igneous: geology - a rock or mineral formed from cooling of molten or partly molten material, such as magma

illite: geology - a general name for a group of triple-layer clays commonly found in marine shales

interbedding: geology - layering of different kinds of sedimentary rock or minerals

intrusive: geology - a rock different from surrounding rock that formed within or forced its way into the surrounding rock

ion: chemistry - an element or molecule dissolved in water with a net positive or negative electrical charge

ion balance: chemistry - a percentage calculation used to check major ions data that compares cations to anions; values near zero suggest that the analysis results are accurate and confirm electroneutrality in the water sample,

ion exchange: chemistry - the chemical reaction process where one ion will replace another in a reaction with a mineral, such as a clay, or a medium containing ionic binding sites

ISO: International Organization for Standardization

IUPAC: International Association of Pure and Applied Chemistry, the organization establishing standardized atomic weights and chemical constants

Jurassic: geology - the second period of the Mesozoic era, after the Triassic and before the Cretaceous, covering a span of time from 135 to 190 million years ago

k: SI unit prefix kilo, or 10^3

K, K^+: chemistry - the element potassium, or potassium ion

kaolinite: geology - a common clay mineral of the kaolin group: $Al_2Si_2O_5(OH)_4$

Kelvin, °K: chemistry/physics - thermodynamic temperature scale with 273° set to the freezing point of water, 373° to the boiling point of water, and 0 °K called absolute zero

K_{eq}, K: chemistry - the equilibrium constant for a given balanced chemical reaction, based on the stoichiometry of the reactions and ratio of product concentrations to reactant concentrations at chemical equilibrium

kg: measurement unit - kilogram, SI mass unit, 1 kg = 1,000 g

kg/d: measurement unit - kilogram per day, used to quantify mass wasting per day in seepage

L: measurement unit - liter, SI volume unit

laminar flow: hydraulic engineering - flow that is slow and uniform

Laramide Orogeny: geology - the period of time when the eastern Rocky Mountains were uplifted and formed, from the late Cretaceous to the end of the Paleocene

lat/long: measurement unit - latitude/longitude

limestone: geology - a sedimentary rock containing more than 50 percent by weight of calcium carbonate; specifically, a carbonate mineral containing at least 95 percent calcite and less than 5 percent dolomite

limnetic: biology/limnology - associated with a lake environment

limnology: the study of the biology, chemistry, morphology, and hydrodynamics of lakes

LOD: chemistry-QA/QC - limit of detection, a statistically based estimate of the lowest statistically valid measurement concentration for an instrument or analytical method

loess: geology - small particle-sized wind-blown deposits

log(AP/KT): chemistry - see saturation index

LOQ: chemistry-QA/QC - limit of quantitation, statistically based. 10 times the standard deviation calculated from repeated same-sample results.

LR: statistics - linear regression

M: chemistry - molarity, moles per liter, ; also SI unit prefix for mega, or 10^6

mafic: geology - pertaining to an igneous rock composed of dark-colored ferromagnesian minerals

magma: geology - naturally occurring mobile molten rock material generated within the earth and capable of extrusion and intrusion; parent material of all igneous rock

magnesite: geology - a carbonate mineral containing magnesium: $MgCO_3$

major ions: chemistry - higher concentration elements dissolved in water, usually: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, CO_3^{2-}, HCO_3^{-}, SO_4^{2-}, and Cl^{-}

Mancos Shale: geology - a sedimentary shale rock formation deposited from inland seas during the middle Cretaceous period, observed throughout the great basin and Colorado, usually observed above the Dakota Sandstone and below the late-Cretaceous to early Tertiary Mesaverde Group coal, sandstones, and mudstones

marble: geology - a metamorphic rock formed from re-crystallized calcite and/or dolomite

mass balance: the quantifying or accounting of mass for materials or chemicals that pass between two or more states

mass balance model: geochemistry - a data analysis method that seeks to explain differences between water concentrations in two or more waters using a set of balanced

mass transport: hydrology - the conveyence of dissolved or supended materials in flowing water

mass wasting: engineering - the transport of solids associated with a structure, foundation, or abutment by water, either through erosion or mineral dissolution

matrix: : : chemistry-QA/QC - the sum of all chemical components in the sample besides the analyte being tested.

matrix spike: chemistry-QA/QC - a real sample to which a known amount of an analyte is added, sometime denoted MS.

MDL: chemistry-QA/QC - method detection limit.

media: chemistry - the type of material associated with a sample: water, wastewater, groundwater, soil, sediments, rock, tissue, etc

meq/L: measurement unit - milliequivalents per liter, 10^{-3} equivalents per liter

mesh: geology/sedimentology measurement unit - a size standard unit based on the diameter of space between the wire mesh in a screen, used to separate and quantify size fractions of solid materials

mesolimnion: limnology - the depth region in a thermally stratified lake where temperature drops to a lower limit in the hypolimnion

metabolism: biochemistry - the biochemical process whereby organisms convert food and nutrients into energy for survival and reproduction

metamorphic: geology - previously formed rock that is transformed in structure and mineralogy at higher pressure and temperature

mg: measurement unit - milligram, SI mass unit, (1 mg = 10^{-3} g)

Mg, Mg^{2+}: chemistry - magnesium, or magnesium ion

mg/kg: measurement unit/chemistry - milligrams per kilogram (1,000 g), SI concentration unit applied to solid samples and liquid samples with high salinity

mg/L: measurement unit/chemistry - milligrams per liter, SI concentration unit

mica : geology - a group of clay-like, layered aluminosilicate minerals that form elastic sheets and flakes in igneous or metamorphic rock

mineral: geology - a rock composed of a single or series of related chemical compounds

mineral dissolution: engineering - the process whereby seepage water dissolves and removes simple minerals in a dam, foundation, or abutments

mineralization: geology - the processes whereby minerals are introduced into rock, and may involve hydrothermal solution processes, fissure filling, impregnation, or replacement

MINTEQ, MINTEQA2: chemistry/geochemistry - a computer chemical equilibrium model developed by EPA that calculates all the possible chemical species in solution based on equilibrium constants for the competing reactions; also calculates mineral saturation indices based on concentrations entered into the model

mL: measurement unit - milliliter, SI volume unit, (1,000 mL = 1.000 L)

mM/L, mmol/L: measurement unit - millimoles per liter, 10^{-3} moles per liter

Mn: chemistry - the element manganese

mol/L, M/L: measurement unit/chemistry - moles per liter

molal: measurement unit/chemistry - moles per 1,000 g of solution,

mole: measurement unit/chemistry - a chemical concentration unit based on the empirical formula of a chemical compound, equal to the mass of Avogadro=s number (6.023×10^{23}) of molecules of a chemical compound, or atoms of an element

monzonite: geology - a group of intrusive plutonic rocks intermediate in composition between syanite and diorite, containing equal amounts of alkali feldspar and plagioclase, and very little quartz

mV: measurement unit - millivolt, (10^{-3} volts) SI voltage unit

mw: chemistry - molecular weight

multivariate: statistics - pertaining to analysis or plots using more than 2 variables

N: chemistry - the element nitrogen; chemistry - normality, expressed in equivalents/liter; Newton, SI unit for force, 10 N = 10 kg-m/s^2,

n: SI unit prefix nano, or 10^{-9}

N/m^2: Newtons per square meter, SI unit for pressure,

Na, Na^+: chemistry - the element sodium, or sodium ion

ND: chemistry-QA/QC - not detected, also U, undetected, or <(number), meaning less than the detection limit.

ng: measurement unit - nanogram, SI mass unit, (1 ng = 10^{-9} g)

ng/kg: measurement unit/chemistry - nanograms (10^{-9} g) per kilogram (1,000 g), an SI concentration unit applied to solid samples and liquid samples with high salinity

ng/L: measurement unit/chemistry - nanograms per liter, SI concentration unit

NH_3: chemistry - ammonia; nitrogen in the -III oxidation state

NH_4^+: chemistry - ammonium ion

NIST: US Department of Commerce - National Institute of Standards and Technology; formerly the National Bureau of Standards

nm: measurement unit - nanometers, (10^{-9} m), usually applied to spectral wavelengths

NO_2^-: chemistry - nitrite, or nitrite ion, nitrogen in the +III oxidation state

NO_3^-: chemistry - nitrate, or nitrate ion, nitrogen in the +V oxidation state

NO_3+NO_2: chemistry - nitrate plus nitrite

NTIS: US Department of Commerce - National Technical Information Service

NTU: measurement unit/chemistry - nephelometric turbidity units

nutrients: chemistry/water quality - a term referring to all nitrogen and phosphorus species, usually includes total-P, ortho-P, TKN, NH_3, NO_2, and NO_3

OH^-: chemistry - hydroxide, or hydroxide ion

Oligocene: geology - an epoch of the early Tertiary period, after the Eocene and before the Miocene

oligoclase: geology - a plagioclase feldspar mineral enriched with sodium, but containing more calcium than albite

oligotrophic: limnology - trophic state of a lake having low productivity, generally higher water transparency, and low concentrations of nutrients and organic carbon

olivine: geology - a group of ferromagnesian silicate minerals formed from igneous rock: $(Mg,Fe,Mn,Ca)_2SiO_4$

ON: chemistry - organic nitrogen

o-P, ortho-P: chemistry - orthophosphate

organic: chemistry - referring to compounds containing carbon, excluding inorganic carbon as in carbonates

Organic-N: chemistry - nitrogen bound to organic matter in water, calculated as TKN - NH_3

orogeny: geology - the process of mountain formation

ORP: chemistry - oxidation-reduction potential; Eh

orthoclase: geology - an alkali feldspar enriched with potassium

oversaturated: chemistry - the temporary condition in a two-phase (solid-solution) system when the reactants in solution that form a chemical compound exceed concentrations required to form the solid compound at equilibrium Oversaturated solutions tend to form the solid product and precipitate out of solution

oxic: biology - an environment containing oxygen; synonym for aerobic

oxidation: chemistry - chemical combination or reaction with oxygen, or removal of electrons to increase oxidation state

oxidizing: chemistry - a chemical environment where oxygen is present and/or excess electrons are unavailable; in natural waters, an aerobic environment where dissolved oxygen is present and compounds may undergo oxidation from a lower oxidation state to a higher oxidation state, such as ferrous iron, Fe^{2+} (Fe in the +II oxidation or valence state), being oxidized to ferric iron, Fe^{3+} (Fe in the +III oxidation or valence state); a natural water environment with positive Eh

oxyhydrate: geology - hydrated oxide/hydroxide minerals usually containing iron and/or manganese

P: chemistry - the element phosphorus; statistics - probability

parameter: statistics - a coefficient for a random variable derived from a statistical analysis.

particulate: chemistry - analytes bound to, or strongly associated with suspended particles in water

pCO_2: chemistry - the partial pressure of carbon dioxide, measured in atm, Pa, or mm of Hg (torr),

percent H_2O: measurement unit - weight percent water

Percent R, %R: chemistry-QA/QC - percent recovery, in general, (observed value))(true value) X 100

percent RSD: statistics - percent relative standard deviation, the ratio of the standard deviation to the mean, expressed as a percentage.

permeability: hydrology/engineering - the property of soil or a geological formation relating to the movement or flow of water in the formation under an applied pressure or head; related to porosity

Permian: geology - rocks formed during the last period of the Paleozoic era, covering a span of time from 225 to 280 million years ago

petrography: geology - the branch of geology that determines the mineralogy of rock and soil

pH: chemistry - hydrogen ion concentration as activity, defined as the negative logarithm (base 10) of the hydrogen ion activity; an indicator of the acidity or alkalinity of water that follows a unitless scale (called su, or standard units) of 0

to 14

phreatic surface: hydrology - the surface of groundwater in an aquifer or earth-fill dam

PHREEQE: chemistry/geochemistry - a computer chemical equilibrium model developed by the USGS that calculates all the possible chemical species in solution based on equilibrium constants for competing reactions based on concentrations and reactions entered into the model

physiography: geology - a description of the surface features and landforms of the earth

phytoplankton: limnology - microscopic plants suspended in water, usually algae and diatoms

piezometer: engineering/hydrology - an instrument that measures the static height of water in a well over time.

Piper diagram: geochemistry - a triangular multivariate graph used to classify waters according to geochmical type using cation and anion concentrations

piping: engineering - fast and erosive flows in a dam, foundation, or abutment, that behave like flow in a pipe and usually lead to structural failure

plagioclase: geology - a group of triclinic feldspar minerals of the general formula: $(Na,Ca)Al(Si,Al)Si_2O_8$

Pleistocene: geology - rocks and deposits formed during the Quaternary period, covering a span of time from 2-3 million to 8,000 years ago

pluvial: geology - referring to a rainy climate

***p*O$_2$**: chemistry - the partial pressure of oxygen, measured in atm, Pa, or mm of Hg (torr),

PO_4^{3-}: chemistry - orthophosphate, phosphate, or phosphate ion

PO_4^{3-}: chemistry - orthophosphate, phosphate, or phosphate ion

***p*OH**: chemistry - hydroxide ion concentration as activity, defined as the negative logarithm (base 10) of the hydroxide ion activity; an indicator of the acidity or alkalinity of water that follows a unitless scale of 0 to 14; pOH = 14 - pH

polygon plot: geochemistry - a graph that plots more than 2 variables with a center value of zero, use to provide a visual shape for classifying samples; examples include Stiff diagrams, radar diagrams

porosity: hydraulic engineering - the ratio of open area to total area of a screen or other porous barrier structure

ppb: measurement unit/chemistry - parts per *billion*, equivalent to :g/kg and usually applied to solid samples and liquid samples with high salinity or density,

ppm: measurement unit/chemistry - parts per *million*, equivalent to mg/kg and usually applied to solid samples and liquid samples with high salinity or density,

ppt: measurement unit/chemistry - parts per *trillion*, equivalent to ng/kg and usually applied to solid samples and liquid samples with high salinity or density; may also be parts per thousand, $^{0}/_{00}$, a unit for salinity

Precambrian: geology - very old rock formed 570 million years ago, or older, before the Paleozoic Era, and composed of the Archeozoic (oldest rocks on the Earth) and Proterozoic (younger rocks)

precipitate: chemistry - to change phase from solution (liquid) to solid or to form an insoluble compound that settles out of solution n a solid compound that settles out of solution

precision: statistics/quality assurance - the repeatability or variability of measurements, usually expressed as a standard deviation or other error

profile: any collection of a measurements made over several cross-sectional units (depth, altitude, elevation, etc); limnology - a plot of water quality variables such as T, DO, or pH with depth, measured at a specific time and location in a water body

pyrite: geology - an iron sulfide mineral, FeS, which creates acidic mine drainage and sulfuric acid when oxidized by exposure to air

q, or Q: hydraulic engineering/hydrology - water flow, measured in volume per unit time, such as m^3/s or ft^3/s (cfs)

QA: chemistry-QA/QC - quality assurance, overall efforts, audits, and tests performed to make sure that sample collectors and the analysis lab are following the QC requirements. These could include lab and field sampling audits, or submission of known concentration samples as blind check samples.

QC: chemistry-QA/QC - quality control, efforts and tests undertaken in the lab to check or document analysis data quality.

qualification: chemistry-QA/QC - a code or commentary describing QA/QC non-conformance and its effect on data usability.

qualitative: chemistry-QA/QC - detected, but not at a high level of precision and/or accuracy.

quantitative: chemistry-QA/QC - detected with a higher degree of precision and accuracy.

quartz: geology - a crystalline silicon dioxide mineral: SiO2

quartzite: geology - a very hard but unmetamorphosed sandstone consisting chiefly of cemented quartz grains

Quaternary: geology - rocks formed during the second period of the Cenozoic Era, following the Tertiary, covering the span of time from 2-3 million years ago to the present time

raw sample: chemistry - a sample that is untreated, unpreserved, or otherwise processed

recovery: chemistry-QA/QC - observed concentration divided by theoretical or true concentration, usually expressed as a percentage.

redox: chemistry - REDuction-OXidation; referring to oxidation-reduction conditions

reducing: chemistry - a chemical environment where oxygen is absent and/or excess electrons are available; in natural waters, an anaerobic environment where compounds may undergo reduction from a higher oxidation state to a lower oxidation state, such as nitrate, NO_3^- (N in the +V oxidation state), being reduced to nitrite, NO_2^- (N in the +III oxidation state), or sulfate SO_4^{2-} (S in the +VI oxidation state), being reduced to sulfide S^{2-} (S in the +II oxidation state); a natural water environment with negative Eh

reduction: chemistry - the chemical removal of oxygen from a compound, or the addition of electrons to lower the oxidation state

regression: statistics - a statistical analysis that compares one or more independent variables, xi, to predict a dependent variable, y

respiration: biology - the process by which an organism obtains oxygen needed to process food into energy

rhyolite: geology - an extrusive igneous rock containing quartz and alkali feldspar

RPD: chemistry-QA/QC - relative percent difference, a way to calculate precision from duplicate analysis data.

S^{2-}: chemistry - sulfide ion, a reduced form of sulfur in the +II oxidation state, found only in anaerobic and reducing natural waters

sandstone: geology - a medium-grained clastic sedimentary rock containing large amounts of quartz, with some clay and cementing minerals

saturated: chemistry - the condition when a chemical compound is in equilibrium with its solid and solution forms

Saturation Index, SI: chemistry/geochemistry - a unitless number pertaining to the chemical reaction of a mineral compound with water, calculated as log(AP/KT), where AP is the activity product, K is the equilibrium constant, and T is the Kelvin temperature The saturation index, calculated by several computer chemical equilibrium models such as MINTEQ and PHREEQE, indicates whether a given natural water is oversaturated (positive numbers), undersaturated (negative numbers), or near equilibrium (values near zero) with a particular mineral phase

screening, sieving: geology/sedimentology - the process of separating solid samples into defined size fractions by sifting the sample through a series of mesh screens

sediment: geology - mineral particles carried by stream flows

seepage: groundwater from an impounded reservoir or lake that flows around a dam or embankment and emerges downstream

seepage chemistry: the properties and concentrations of chemical constituents present in a seepage water, usually the major ions, organic carbon, nitrogen and phosphorus, and several trace elements. Also includes pH, conductivity, and redox potential.

seepage transit: the period of time or the process required for seepage to leave the reservoir, enter the abutment or foundation geology, and then emerge downstream.

shale: geology - a fine-grained and laminated detrital sedimentary rock composed of fine silt and clay, or mud; also called claystone, mudstone

Si: chemistry - silicon (element)

SI: measurement unit - Système Internationale d=Unités, the international standard system for metric measurement units; geochemistry - saturation index

silica: geology - amorphous silicon dioxide mineral: SiO2

silicate: geology - a mineral containing SiO4

sill: geology - a tabular igneous intrusion that parallels the planar structure of the surrounding rock

silt, silt-sized: geology/sedimentology - soil or sediment particles ranging from 0.002 to 0.05 mm in diameter; a particle size class smaller than fine sand but larger than clay-sized particles

SiO_2: chemistry - silica (mineral)

SiO_4, SiO_3^{2-}: chemistry - silicate, silicate ion

slurry: chemistry - a mixture of solid materials in a liquid

smectite : geology - a group of multi-layered clay minerals with swelling properties and high cation exchange capacity Also called montmorillonite

SO_4^{2-}: chemistry - sulfate, or sulfate ion, the dominant form for sulfur in oxygenated natural waters

soil: geology - geological materials capable of sustaining plant growth

solute: chemistry - the chemical that is dissolved into the solvent

solvent: chemistry - the chemical that dissolves the solute

SOP: QA-QC - Standard Operating Procedure

speciation: chemistry - the description of the different compounds formed by an element in a natural water

species: chemistry - the term applied to different compounds that are formed with elements in natural water

spectrometer: chemistry - an instrument that measures light intensity at different wavelengths

spectrophotometric: chemistry - an analytical technique that determines analyte concentration by measuring light transmission, emission, or adsorption, at given wavelength

spike: chemistry-QA/QC - a known amount of an analyte added to a real sample or blank.

spinel: geology - a group of ferromagnesian minerals: AB_2O_4, where A can be any or all of Mg, Fe^{2+}, Fe^{3+}, Zn, or Mn, and B can be oxides of Al, Fe^{2+}, Fe^{3+}, or Cr

SRM: chemistry-QA/QC - standard reference material, a known-concentration standard, usually manufactured and tested by a national standards organization (such as NIST.)

SSSA: Soil Science Society of America

stocks: geology - an igneous intrusion that is less than 100 km^2 in size

stoichiometry: chemistry - the set of coefficients for reactants and products in a chemical reaction that produce a balanced algebraic equation and condition of mass balance between reactants and products

STP: chemistry - standard temperature and pressure, equal to 1 atm and 273 °K (0 °C)

strata (pl): geology - adjacent rock layers or laminar deposits associated with sedimentary rocks

strike, line of strike: geology - the direction or trend taken by a structural surface; to be alligned or trend in the direction perpendiculr to the line of dip.

su or s.u.: measurement unit/chemistry - standard units, usually applied to pH

subsample: sampling/QA - a portion of a larger sample collected to represent the larger sample or population

supernate: chemistry - the liquid separated from a slurry during centrifugation

suspended: chemistry - an operationally defined term applied to water analysis results; analytes associated with suspended particles larger than 045 :m, usually calculated by subtracting dissolved from total

T: chemistry - temperature, °C

TDS: chemistry - total dissolved solids, mg/L, also called Afilterable residue@

Tertiary: geology - the first period of the Cenozoic era, covering the span of time between 2-3 million and 65 million years ago

thermal stratification: limnology - the tendency for deeper lakes to form temperature and density layers in the water column,

thermocline: limnology - the temperature transition zone in a thermally stratified lake, associated with the depth of the mesolimnion

thermodynamic: chemistry - pertaining to the study of heat transfer and the formation and breaking down of chemical compounds

titration: chemistry - the process of adding a standardized reactant chemical solution to a liquid sample, and monitoring completion of a reaction that forms a detectable product

titrimetric: chemistry - an analytical method that uses a titration

TKN: chemistry - total Kjeldahl nitrogen, an digestion analysis that detects both ammonia and organic nitrogen

TM: chemistry - trace metals

TOC: chemistry - total organic carbon

TON: chemistry - total organic nitrogen

total: chemistry - an operationally defined term applied to water analysis results, usually meaning an unfiltered sample that is digested or extracted prior to analysis

t-P, total-P: chemistry - total phosphorus

trace: chemistry - low concentrations, generally from mg/L to many :g/L

trace elements: chemistry - a general term applied to low concentration (less than a mg/L) transition metals such as Fe, Pb, Hg, Cd, Cu, Zn, and other elements such as As, Se, and Mo; sometimes called trace metals or toxic metals

trace metals: chemistry - a general term for low concentration trace elements

traceable: chemistry-QA/QC - usually refers to a check sample or verification sample with known values and a certificate indicating comparison to a standard reference material.

travertine: geology - a carbonate mineral formed by rapid precipitation, usually when groundwater super-saturated with calcium and carbonate contacts a flowing stream

travertine cones: geology - conical solid deposits of travertine that form in stream beds

Triassic: geology - the first period of the Mesozoic era (after the Permian period of the Palaeo and before the Jurassic) ranging from 190 to 225 million years ago

trophic state: limnology - a classification of a lake with respect to biological productivity High productivity lakes are classified as eutrophic, low productivity lakes as oligotrophic

TSC: Technical Service Center, Bureau of Reclamation, Denver, Colorado

TSS: chemistry - total suspended solids, mg/L, also called "nonfilterable residue"

tuff: geology - a general term for consolidated pyroclastic or volcanic rocks

tuffaceous: geology - containing tuff

turbidity: chemistry - particulate matter in water that scatters light causing a cloudy appearance

turbulent flow: hydraulic engineering - flow that is fast, complex, and chaotic

turnover: limnology - the mixing of a thermally stratified lake, usually occurs in spring and fall

TV: chemistry-QA/QC - true value.

undersaturated: chemistry - the condition in a two-phase (solid-solution) system when the reactants in solution that form a chemical compound are below concentrations required to form the solid compound Undersaturated solutions tend to dissolve the solid reaction product

uplift: geology - a structurally high area in the crust, produced by movements that raise or upthrust the rock

USBR, BOR: US Department of the Interior - Bureau of Reclamation

USGS: US Department of the Interior - Geological Survey

valence: chemistry - the oxidation state of an element, usually denoted by Roman numerals, as Fe(+III) or S(+VI); valence is used to calculate equivalent weight

variable: statistics - a measured property that varies.

vermiculite: geology - a group of platey or micaceous clay minerals closely related to chlorite and montmorillonite, also the weathering products of micas Has a general formula: (Mg,Fe,Al)3(Al,SI)4O10(OH)2@ 4H2O

void: engineering - an empty space formed in a solid structure

volatile: chemistry - a solid or liquid with a tendency to evaporate or sublimate into the gas phase

volcanism: geology - the processes by which magma rises to the surface of the earth=s crust and is extruded

water type: geochemistry - a classification of water based on its dominant cations and anions

weathering: geology - the process whereby exposed rock is degraded, eroded, or chemically decomposed by exposure to air, water, sunlight, heat and cold; the process whereby one mineral is converted to another

WEF: Water Environment Federation

wetland: biology - an area that collects water during part or all of the year

zeolite: geology - a large group of white or colorless aluminosilicate minerals similar to feldspars, usually associated with volcanic tuffs Zeolites also possess ion exchange capacity

Zn: chemistry - the element zinc

µ: statistics - Greek letter mu; the population mean; SI metric unit prefix for micro, or 10^{-6}

µeq/L: measurement unit/chemistry - microequivalents per liter, 10^{-6} equivalents per liter

µg: measurement unit/chemistry - microgram, SI mass unit, 1 :g = 10^{-6} g

µg/kg: measurement unit/chemistry - micrograms per kilogram (1,000 g), an SI

concentration unit applied to solid samples and liquid samples with high salinity,

µg/L: measurement unit/chemistry - micrograms (10^{-6} g) per liter, SI concentration unit,

µm: measurement unit - micrometer, or micron (10^{-6} m), SI length unit

µM/L, µmol/L: measurement unit/chemistry - micromoles per liter, 10^{-6} moles per liter

µS/cm: measurement unit/chemistry - microsiemens per square centimeter, an SI unit for electrical conductivity,

ρ: Greek letter rho; chemistry/physics - density, measured in g/cm^3 at STP

Unit Conversion Factors

Conversion factors are from the Bureau of Reclamation's *Metric Manual*, 1978, by L.D. Pedde, W.E. Foote, L.F. Scott, D.L. King, and D.L. McGalliard, U.S. Government Printing Office, Washington DC. English weights and volumes are *avoirdupois* units, and English volumes are based on fluid ounces.

Metric Prefixes
pico = p = 10^{-12}
nano = n = 10^{-9}
micro = μ = 10^{-6} = 0.000001
milli = m = 10^{-3} = 0.001
centi = c = 10^{-2} = 0.010
hecto = h = 10^{+2} = 100
kilo = k = 10^{+3} = 1,000
mega = M = 10^{+6} = 1,000,000
giga = G = 10^{+9}
tera = T = 10^{+12}

Length
1.0 inch = 0.0254 m = 2.54 cm = 25.4 mm
1.0 foot (ft) = 0.30480 m = 30.480 cm = 304.8 mm
1.0 yard (yd) = 0.91440 m = 91.440 cm = 914.4 mm
1.0 mile (mi) = 1,760 yd = 5,280 ft = 63,360 in = 1.6093 km = 1,609.3 m = 160,934 cm
1.0 cm = 0.010 m = 10 mm = 0.03281 ft = 0.3937 in
1.0 meter (m) = 100 cm = 1,000 mm = 1.0936 yd = 3.2808 ft = 39.370 in
1.0 km = 1,000 m = 100,000 cm = 0.62137 mi = 1,093.61 yd = 3,280.83 ft = 39,370 in

Weight
1.0 gram (g) = 1,000 mg = 1,000,000 μg = 1.000 cm^3 deionized H_2O at STP
1.0 kg = 1,000 g = 2.204622 lb = 35.27396 oz
1.0 ounce (oz) = 0.06250 lb = 28.34953 g = 0.0283495 kg
1.0 pound (lb) = 16 oz = 0.45359 kg = 453.59 g

Time
1.0 hour = 3,600 s
1.0 day = 1,440 min = 86,400 s
1.0 week = 168 hr = 10,080 min = 604,800 s

Temperature

Celsius to Fahrenheit: **°F = (°C x 1.80) + 32**
Fahrenheit to Celsius: **°C = (°F - 32) x 0.5556**
Kelvin to Celsius: **°C = °K - 273.15**
Celsius to Kelvin: **°K = °C + 273.15**
STP - standard temperature and pressure = 273 °K at 1 atm

Area

1.0 in^2 = 0.00064516 m^2 = 6.4516 cm^2 = 645.16 mm^2
1.0 ft^2 = 0.1111 yd^2 = 144 in^2 = 0.092903 m^2 = 929.03 cm^2 = 92,903 mm^2
1.0 yd^2 = 9 ft^2 = 1,296 in^2 = 0.836127 m^2 = 8,361.27 cm^2 = 836,127 mm^2
1.0 acre = 0.0015625 mi^2 = 4,840 yd^2 = 43,560 ft^2 = 4,046.87 m^2= 0.404687 ha
1.0 mi^2 = 640 acres = 27.878 x 10^6 ft^2 = 2,589,988 m^2 = 258.99 ha
1.0 cm^2 = 100 mm^2 = 0.1550 in^2
1.0 m^2 = 10,000 cm^2 = 1.1959 yd^2 = 10.7369 ft^2 = 1,550.0 in^2
1.0 hectare (ha) = 100 m x 100 m = 10,000 m^2 = 0.00385901 mi^2 = 2.47104 acres = 11,959.9 yd^2
1.0 km^2 = 100 ha = 1,000,000 m^2 = 0.3860 mi^2 = 247.104 acres

Volume

1.0 fluid oz = 1.8047 in^3 = 0.029574 L = 29.574 mL
1.0 in^3 = 0.5541 oz = 0.016387 L = 16.387 mL
1.0 pint = 16.0 fluid oz = 0.47318 L = 473.18 mL
1.0 quart = 2.0 pt = 32.0 fluid oz = 0.94635 L = 946.35 mL
1.0 gallon = 4.0 qt = 8.0 pt = 128 fluid oz = 3.7854 L
1.0 ft^3 = 7.4805 gal = 0.028317 m^3 = 28.317 L
1.0 acre-ft = 1233.489 m^3 = 1.233 X 10^6 L = 325,851 gal
1.0 cm^3 = 1.0 mL deionized H_2O at STP = 0.001 L
1.0 liter (L) = 0.001 m^3 = 1,000 mL = 0.264172 gal = 1.0567 qt = 2.1134 pt
1.0 m^3 = 1,000 L = 8.1071 x 10^{-4} acre-ft = 35.315 ft^3 = 264.17 gal

Flow

1.0 gal/min (gpm) = 0.0044191 acre-ft/d = 0.0022280 cfs = 192.5 ft^3/d = 3.7854 L/min= 0.063090 L/s = 227.124 L/hr = 5,451 L/d
1.0 ft^3/s (cfs) = 1.98347 acre-ft/d = 448.831 gal/min = 646,317 gal/d = 0.0283169 m^3/s= 28.3169 L/s = 2.4466 x 10^6 L/d = 2,446.6 m^3/d = 1,699.01 L/min = 101,941 L/hr
1.0 acre-ft/d = 0.504167 cfs = 325,851 gal/d = 14.2764 L/s = 856.584 L/min= 51,395 L/hr = 1.23348 x 10^6 L/d = 1,233.482 m^3/d
1.0 m^3/s = 1,000 L/s = 35.315 ft^3/s = 264.17 gal/s
1.0 L/s = 1,000 mL/s = 0.0010 m^3/s = 0.035315 ft^3/s = 0.264172 gal/s

Chemical Concentrations

1.0 mg/L = 0.001 g/L = 1,000 µg/L = 1,000,000 ng/L
1.0 µg/L = 0.001 mg/L = 1,000 ng/L
1.0 ng/L = 0.001 µg/L = 0.000001 mg/L

1.0 percent = 1.0 g/100g = 10 ^{o}/oo (parts per thousand) = 10 g/kg = 10,000 mg/kg(also applies to units/L for dilute waters with low TDS and D ~ 1.0 g/cm^3)
1.0 g/kg = 0.10 percent = 1,000 mg/kg
1.0 mg/kg = 0.0010 g/kg = 0.00010 percent = 1,000 μg/kg
1.0 μg/kg = 0.001 mg/kg = 1,000 ng/kg