MINERAL DISSOLUTION AND DAM SEEPAGE CHEMISTRY - THE BUREAU OF RECLAMATION EXPERIENCE

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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 paper 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. The paper includes a guide to planning seepage chemistry investigations, and includes examples from successful seepage investigations performed over the past 20 years by Bureau of Reclamation Dam Safety Program professionals.

Introduction

This paper provides engineers and non-chemists 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, and an overview of geochemical interpretation techniques routinely applied to seepage chemistry data. An expanded version of this paper with additional detail and resources is available from the first author [1].

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 [2], that provide water for agricultural, residential, municipal, and industrial uses to more than 31 million people in the arid West.

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 [3]. Reclamation's dam safety activities are also coordinated under the National Dam Safety Program managed by the Federal Emergency Management Agency (FEMA) [4].

Seepage and Dam Failures

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 foundation materials (with large flow cross sections) usually experience longer transit times and behave more like a typical groundwater. Both confined and diffuse seepage paths will exhibit time-lagged flow response to changes in reservoir head. Seepage flow may not increase immediately when reservoir elevation rises, and some seeps will flow well after reservoir elevation has dropped. In general, a seep that responds quickly to reservoir elevation changes suggests a direct hydraulic path from the reservoir to the seep that should be monitored carefully.

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.

> *All dams leak.*
> William Mulholland, March 11, 1928, while inspecting seepage at St. Francis Dam [5]

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 disastrous 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 forming voids, 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 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 over geologic time when groundwater dissolved the mineral calcite ($CaCO_3$) and left behind void spaces [6].   Dams accelerate the rate of dissolution by increasing seepage flow velocity.

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 concrete and earthen dams have often been associated with structural failure and downstream flooding [7,8,9,10,11,12], so determining the extent and nature of mineral dissolution should be a priority in dam safety assessments where seepage is a concern.

The Chemistry of Solubility

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 by Reclamation to help evaluate mineral dissolution since 1951, when downstream seeps began flowing after first filling of the reservoir at Horsetooth Dam, Fort Collins, Colorado.

Primary Variables Affecting Mineral Solubility

There are two primary variables associated with water that affect the solubility of minerals and other solutes: pH and redox potential.

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). The pH scale varies from 0 to 14, with values < 7 representing acidic conditions, and values > 7 representing basic or alkaline conditions, and pH of 7 is considered neutral. Acidic waters will dissolve solutes that are bases, and alkaline waters will dissolve acidic solutes. The pH of pure water in equilibrium with the atmosphere is < 7, caused by dissolved CO_2 forming bicarbonate ion (HCO_3^-), carbonic acid (H_2CO_3), and H^+. Rain is therefore slightly acidic and will tend 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 (or concentration) of free electrons ($[e^-]$) in water and is analogous to pH. A *reducing* water has an abundance of $[e^-]$, while an *oxidizing* water has very low $[e^-]$. (Free electrons and protons do not actually exist in water, but the concept is useful.) In natural waters, redox is actually controlled by two primary influences: mixing with O_2 from the atmosphere (dissolved oxygen, DO), and bacterial activity. Water can be *oxidizing* or *reducing* (analogous to acidic and basic), and each redox state will encourage specific reactions.

Water containing DO is oxidizing, and these conditions will favor the breakdown of organic compounds, precipitation of iron (Fe) and manganese (Mn) as insoluble compounds called oxyhydrates, formation of chemical species with higher oxidation states (Fe^{3+} in the +III oxidation state, Mn^{4+} in the +IV state, CO_2 with C in the +IV state, nitrate, NO_3^- with N in the +V state, and sulfate, SO_4^{2-} with S in the +VI state; and dissolution of reduced solutes such as pyrite, ferrous sulfide (FeS_2^2) - the acid mine drainage reaction [13]. 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 dissolved trace elements, and chemical species with *lower* oxidation states such as Fe^{2+} (+II), Mn^{2+} (+II); CH_4 (C in the -IV state); ammonia, NH_3 (N in the -III state); and sulfide, S^{2-} (S in the -II state).

Other Factors 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 new solute. Temperature and pressure affect solubility. Generally, the solubility of electrolytes and solid non-electrolytes 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's 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

Equilibrium Concepts and Solubility Classes

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

$$NaCl \overset{\text{halite}}{\underset{}{\leftrightarrows}} \overset{H_2O}{} Na^+ + Cl^-$$

Equation 1

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.

With mineral dissolution, solubility is 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 under saturated. If solute is added over and above this amount, it will remain as a solid phase with liquid and will not dissolve into solution. When solid solute co-exists 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 over saturated solution. Given time, a solute will usually precipitate (form the solid compound) out of an over saturated solution.

Reservoir water contains previously dissolved cations, anions, and other trace inorganic and organic compounds, and water having higher concentrations of solutes will be less able to dissolve minerals during seepage transit. Reservoir water will also become more concentrated as it flows beneath the dam and dissolves minerals, so seepage water can become less aggressive dissolving minerals towards the end of its transit. Initial concentrations of reservoir water will also vary with season and depth because of thermal and chemical stratification. During winter and summer, when deeper reservoirs will stratify, higher concentration water will sink to the bottom where seepage often begins its foundation transit. Seepage flow beneath a dam will fluctuate depending on reservoir surface elevation and hydraulic head between reservoir and tailwater, so seepage residence time will vary during the year.

Some dissolution reactions are fast, but many involving minerals are slow and 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 [14,9]. 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 grams per liter (g/L). These minerals are usually called *evaporites* because they formed as paeleo-ocean and -lake waters evaporated. They are usually associated with sedimentary deposits and artesian hydrothermal springs in volcanic rocks. 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, $Na_2B_4O_7 \cdot 10H_2O$).
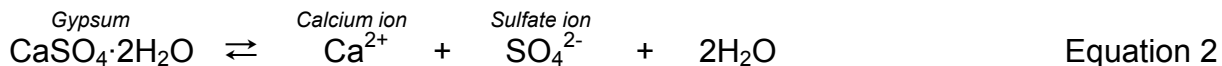
Soluble
Solubilities on the order of 0.5 to 10 g/L (500 to 10,000 mg/L). These minerals may be evaporites or precipitates. Examples include gypsum (calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$), anhydrite (anhydrous calcium sulfate, $CaSO_4$), and villiaumite (sodium fluoride, NaF).

Sparingly Soluble
Solubilities on the order of 0.001 g/L to 0.50 g/L (5 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).

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 diopside ($CaMgSi_2O_6$), chlorite ($Mg_5Al_2Si_3O_{10}(OH)_8$), hornblende ($Ca_2Mg_4AlSi_7O_{22}(OH)_2$) anorthite (calcium aluminosilicate, $CaAl_3Si_2O_6$), 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 will be. Table 1 provides a summary of published solubilities and densities for typical minerals in each of the different solubility classes used in this report [15,16,17,18]

Weathering and Water Quality

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 surface rocks is for the relatively simple, lower-molecular weight, and crystalline feldspars and quartz minerals to break down, liberating free ions that may dissolve into surface waters and also form other minerals. These minerals also weather and eventually form clays. There are two primary weathering processes that affect minerals and seepage: *congruent* and *incongruent* dissolution.

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:

$$\underset{\text{Gypsum}}{CaSO_4 \cdot 2H_2O} \; \rightleftharpoons \; \underset{\text{Calcium ion}}{Ca^{2+}} \; + \; \underset{\text{Sulfate ion}}{SO_4^{2-}} \; + \; 2H_2O \qquad\qquad \text{Equation 2}$$

$$\underset{\text{Anhydrite}}{CaSO_4} \; \rightleftharpoons \; \underset{\text{Calcium ion}}{Ca^{2+}} \; + \; \underset{\text{Sulfate ion}}{SO_4^{2-}} \qquad\qquad \text{Equation 3}$$

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

$$\underset{\text{Calcite}}{CaCO_3} + H_2O + CO_2 \; \rightleftharpoons \; Ca^{2+} \; + \; \underset{\text{Bicarbonate ion}}{2HCO_3^-} \qquad\qquad \text{Equation 4}$$

$$\underset{\text{Magnesite}}{MgCO_3} + H_2O + CO_2 \; \rightleftharpoons \; Mg^{2+} \; + \; \underset{\text{Bicarbonate ion}}{2HCO_3^-} \qquad\qquad \text{Equation 5}$$
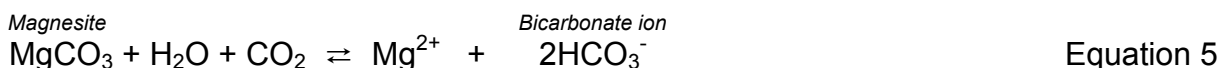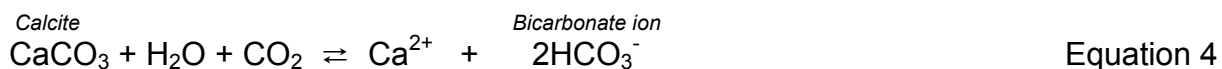
Table 1 - Reported aqueous solubilities and densities for some simple and complex minerals arranged by solubility class. Values are from several sources and represent generally neutral pH water as the solvent [15,16,17,18,19,20].

Solubility Class	Mineral Name or Class	Chemical Name - or Example Minerals	Chemical Formula	Solubility, g/L	Density, g/cm³
Very Soluble	Antarcticite	calcium chloride hexahydrate	$CaCl_2 \cdot 6H_2O$	1,620	1.71
	Bischofite	magnesium chloride hexahydrate	$MgCl_2 \cdot 6H_2O$	1,190	1.56
	Hexahydrite	magnesium sulfate hexahydrate	$MgSO_4 \cdot 6H_2O$	948	1.76
	Epsomite	magnesium sulfate septahydrate	$MgSO_4 \cdot 7H_2O$	757	1.67
	Mirabilite	sodium sulfate decahydrate	$Na_2SO_4 \cdot 10H_2O$	670	1.46
	Natron (Washing Soda)	sodium carbonate decahydrate	$Na_2CO_3 \cdot 10H_2O$	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	$Na_3PO_4 \cdot 12H_2O$	280	1.60
	Trona (Baking Soda)	sodium bicarbonate-carbonate dihydrate	$Na_3(HCO_3)CO_3 \cdot 2(H_2O)$	100	2.13
	Borax	sodium borate decahydrate	$Na_2B_4O_7 \cdot 10H_2O$	62.5	1.73
Soluble	Villiaumite	sodium fluoride	NaF	4.3	2.78
	Gypsum	calcium sulfate dihydrate	$CaSO_4 \cdot 2H_2O$	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: kaolinites: illites:	$(Ca,Na)_{2\,0.7}(Al,Mg,Fe)_4[(Si,Al)_8O_{20}](OH)_4 \cdot nH_2O$ $Al_4[Si_4O_{10}](OH)_8$ $K_{(1.5-1.0)}Al_4[Si_{(6.5-7.0)}Al_{(1.5-1.0)}O_{20}](OH)_4$	- - -	2 - 3 2.61 - 2.68 2.6 - 2.9

$$\underset{Dolomite}{CaMg(CO_3)_2} + H_2O + CO_2 \rightleftarrows Ca^{2+} + Mg^{2+} + \underset{Bicarbonate\ ion}{2HCO_3^-} \qquad \text{Equation 6}$$

Dam safety professionals should be concerned with the congruent reactions in Equations 2-6 because of the extensive presence of limestone and sedimentary evaporite deposits in the United States, and the structural risk posed by void formation in the abutments and foundations of dams. These risks are exacerbated when the foundation rocks of dams include limestone and gypsum in *karst* formations. Karst formations 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 formations containing calcite and gypsum

deposits [8,9,10,21]. Calcite, silica, and other soluble minerals can also be present as cementing agents in sandstones, mudstones, and shales, so seepage may increase abutment or foundation permeability over time even when these soluble minerals will not form large void spaces.

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. Potassium feldspar (orthoclase) weathering to form the clay kaolinite is an example of incongruent dissolution [22,23], 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+} [23].

These reactions are common, but may be very slow relative to seepage residence times in a dam structure [24]. Incongruent dissolution may increase or decease ion concentrations (notably HCO_3^-, Al, and SiO_2) in seepage; however, its contribution to seepage concentration increases is usually on the order of < 5 percent of total change in concentration. In some cases, an incongruent mineral reaction may actually reduce the amount of particular reactants, such as seen for H_4SiO_4 and Ca^{2+} in Equation 8. The formation of void spaces from incongruent dissolution is also not certain. Depending on the densities of the parent and weathered minerals, swelling and reduction of seepage flow may also occur.

Water Quality and 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 the 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). Alkalinity is sometimes reported as "mg/L as $CaCO_3$". The major ions usually occur in the many milligram per liter (mg/L) or milliequivalent per liter (meq/L) concentration range, and comprise what is usually referred to as general water quality.

Trace and Ultra-Trace Constituents - Besides the major ions, trace constituents (at concentrations around 1 mg/L and less) 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) ultra-trace 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 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 [25].

Summarizing Water Quality - Often, water quality is summarized as the sum of dissolved constituents, called total dissolved solids (TDS) [19]. 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 will approximate the TDS by evaporation. TDS will generally increase 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 (> 3,000 m, 9,800 ft.),

TDS can vary from <20 to 100 mg/L. In lower elevation waters, such as Lake Powell (elevation ~ 3,500 ft, 1,070 m), TDS ranges from 500 to 1,000 mg/L [26].

Another useful variable describing the overall concentration of waters is electrical conductivity, EC, measured in microSiemens per centimeter, µS/cm. Waters containing dissolved electrolytes will conduct electricity in proportion to concentration; however, as water becomes more concentrated, charged electrolytes in solution will tend to form ion pairs that do not contribute to EC. Thus, the relationship between EC and ion concentration is not linear. Generally, EC in µS/cm will approximate TDS and sum of ions in mg/L, and can be used to check overall analysis quality [27].

A good way to visualize major ions and trace concentration data is to use polygon plots, such as Stiff [28], Piper [29], 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 Data Interpretation section below.

Figure 1 - Polygon plots are helpful ways to visualize seepage water major ions chemistry data. Below left is a Stiff diagram [28] 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 [29] (below center) plot major ions data and are used to classify the geochemical type of seepage water.
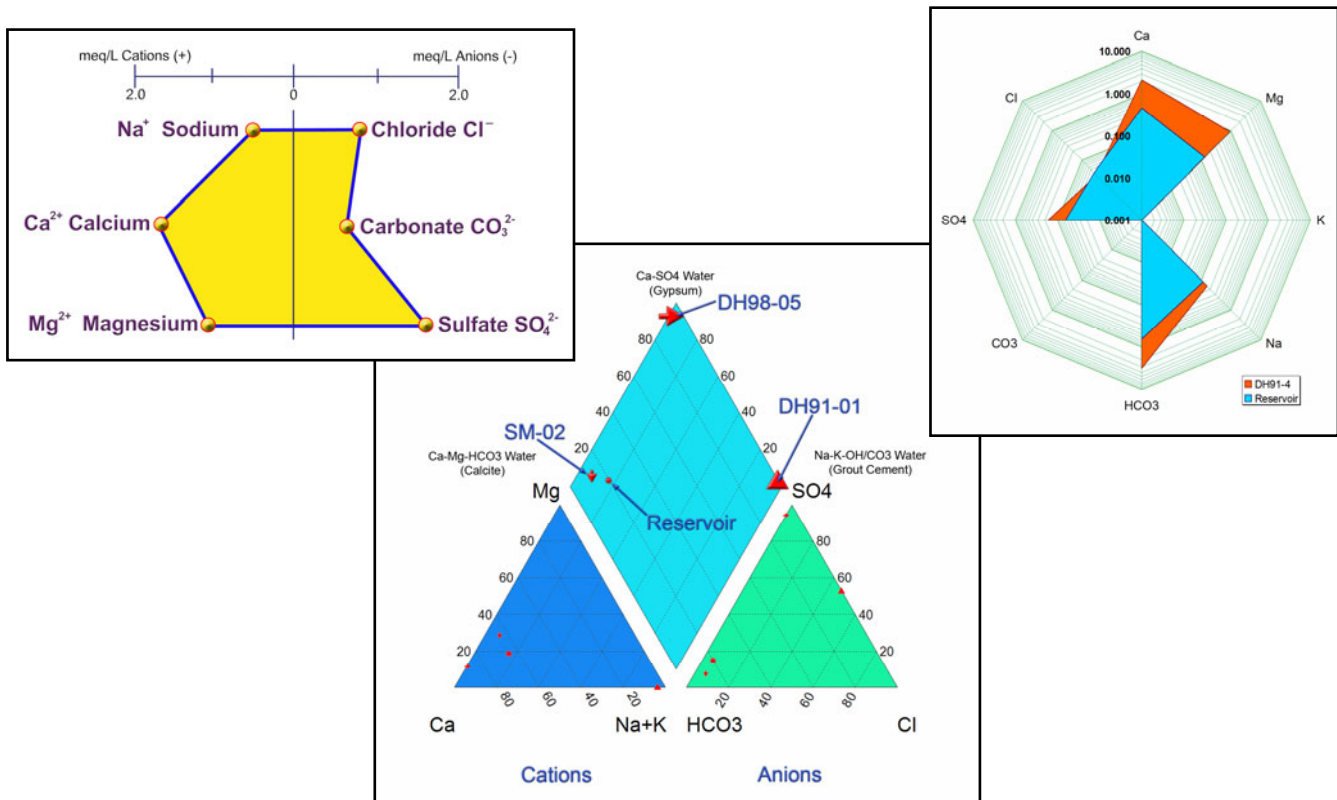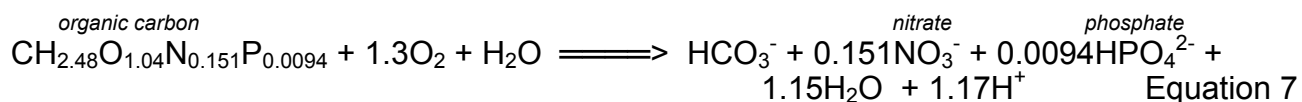
Other Processes Affecting Seepage Chemistry

Just because seepage 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 that simple flow-weighting calculations might suggest.

Biotic Processes - Water quality is strongly affected and changed by living microorganisms that use carbon and oxygen [30]. 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 [13,31]. 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 bacterial, algal and other microorganisms at the base of the aquatic food chain. Reservoirs with elevated OC and high primary productivity (*eutrophic* systems) will form a richer culture medium for bacteria compared to lower productivity reservoirs (*oligotrophic* systems).

Seepage starts as a surface water and then becomes a groundwater once it begins to move beneath or around a dam. Surface waters mixed with the atmosphere will have a constant source of fresh O_2, but underground, the supply of DO will gradually be depleted by bacteria [32,33]. The general reaction for the bacterial oxidation (breakdown or metabolism) of organic carbon is as follows [23,25]:

$$\underset{\text{organic carbon}}{CH_{2.48}O_{1.04}N_{0.151}P_{0.0094}} + 1.3O_2 + H_2O \Longrightarrow HCO_3^- + 0.151\underset{\text{nitrate}}{NO_3^-} + 0.0094\underset{\text{phosphate}}{HPO_4^{2-}} +$$
$$1.15H_2O + 1.17H^+ \qquad \text{Equation 7}$$

For each organic carbon molecule, 1.3 molecules of O_2 are reduced, forming HCO_3^- (an aqueous proxy for CO_2). The byproducts of this reaction includes some nitrate (NO_3^-), phosphate (PO_4^{3-}), and acidity (H^+). Here is where the impact from biotic processes becomes more important to seepage chemistry. 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 2 shows lower dissolved OC (DOC) concentrations in seeps and weirs compared to reservoir samples measured at Deer Flat Embankments [34], showing measurable changes in OC suggesting that biotic processes are likely.

Table 2 - DOC concentrations (mg/L as C) measured at reservoir 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

Because seepage is a groundwater and DO cannot be replenished, bacteria will begin to change concentrations once seepage water enters the foundation or abutments, and redox conditions will change in a predictable manner. First, aerobic and facultative bacteria deplete the available DO. Then a sequence of facultative bacteria (bridge species able to respire under aerobic and anaerobic conditions) 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 is depleted. At each stage, the system becomes more reducing and measured Eh will become increasingly negative. In groundwaters and seepage (as well as bottom waters in stratified lakes), the sequence of bacterial respiration/reduction proceeds as follows [23,31,34,35,36]: DO depletion, nitrate (NO_3) depletion and denitrification, reduction of Mn- and Fe-oxyhydrates, reduction of sulfate to sulfide, methanogenesis (CO_2 reduction to methane, CH_4).

So, biotic processes will contribute more to concentration increases with longer seepage residence times and adequate substrate for metabolism and respiration. Investigations at Deer Flat Embankments, Caldwell, Idaho, 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 that must seep first though a thick coating of organic muck and reducing sediments before entering the embankment foundations [34].

Ion Exchange - Clays, usually smectites and illites, constitute most of the upper surface layers of basin soils, and are also used as embankment materials in earthen dams. Clays are sheet-like aluminosilicate minerals that can form layers loosely held together by Ca, Mg, Na, and K ions [20,37]. These interlayer cations are not strongly bound, and experience a reaction called *ion exchange*. If the local runoff and groundwater contain larger proportions of Ca compared to Na, Ca will exchange for Na in the clay lattice (in a Na-montmorillionite, for example), and thus increase Na concentration in the pore water [38,39].

Mixing and Hydrologic Factors

The last factors that needs to be considered involves the hydrologic variables affecting seepage chemistry at a dam.

Mixing - 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 [40,41], and the groundwater aquifer that existed prior to the dam and reservoir may continue to seep into and mix with reservoir derived seepage.

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 [42,43]. Various mixing programs, such as NETPATH [44] 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 stable isotopes ^{2}H, ^{13}C, ^{18}O, ^{15}N, and ^{34}S using isotope ratio mass spectrometry. Recent surface waters and different groundwaters have varying ratios of the stable isotopes that may be use to identify and distinguish different sources, mixing ratios, and even seepage flow rate and residence time [45,46,47,48]

Delayed Structural Flows - Finally, delayed flow of seepage around the abutments of a dam may account for increases in seepage concentrations. At Glen Canyon Dam, concern was expressed by public advocacy groups about potential mineral dissolution when seepage emerging at a downstream canyon wall was seen with elevated concentrations compared to same date reservoir surface samples. A study of seepage at Glen Canyon Dam [26] using the MODFLOW groundwater flow model [49] suggested that seepage flowed horizontally around the dam and estimated residence times of around 6 months. Additionally, Lake Powell, which varies between 350 to 500 ft 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 (figure 2).

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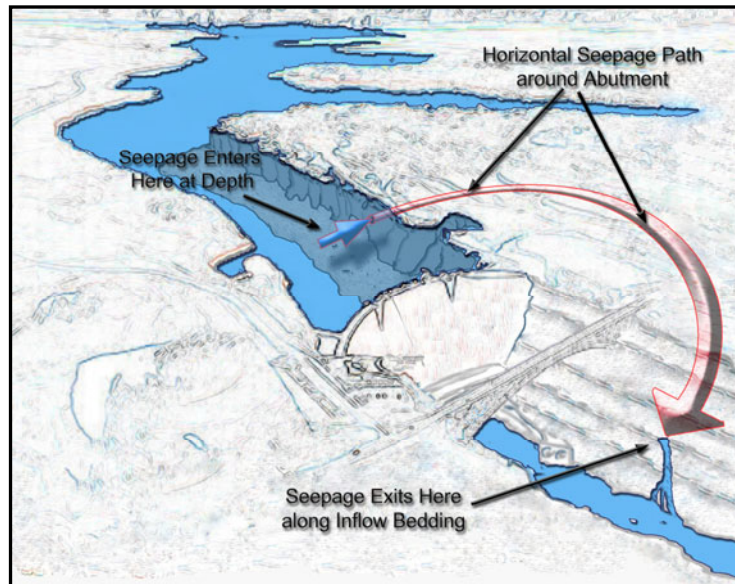
An important conclusion from the Glen Canyon Dam study is that seeps closer to the dam are more important for seepage chemistry assessments because 1) they are closer to foundation and abutments and have greater potential structural implications; and 2) they are likely more direct flow paths lacking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

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 means 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 could be a warning sign.

Mineral Dissolution and Dam Seepage

Because of the hydraulic heads associated with reservoirs and the heterogeneity and fractures in foundation rocks, all dams leak and have seepage [7]. 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 will begin to flow around the abutments and through the foundation. In the case of earthen dams, water will also begin to flow though the embankment. If the foundation and abutments are fairly uniform and unfractured, seepage flows will 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 will 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 [7,12]. Much higher seepage concentrations compared to recent samples were observed at Horsetooth Dam in the 1951 post filling SM-3 samples, that emerged from a limestone karst outcrop 3,000 ft. downstream of the dam [50]. Initial filling at Horsetooth Dam produced a new reservoir-dominated aquifer that contacted previously undissolved geologic strata and mobilized readily available soluble minerals.

Seepage in Formations with Minimal Soluble Minerals - In the real world, rock formations are not uniform - even in massive sandstones such as those at Glen Canyon Dam. Seepage flow will follow 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 will dissolve and increase the permeability of the structural rock in sandstones, porous volcanic rock, and other non-limestone sedimentary rocks.   Often, these seeps can become steady state flows that do not increase 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 formations. 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 created structural slumping, piping, and dam failures [11,12]. In many karst systems, the groundwater flow cannot be characterized as a typical aquifer, but rather as a network of underground streams. Karstic strata often 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.

The progression of void formation in karst has been studied extensively for many years [9,51,52,53], and fundamentally, void paths are likely to enlarge over time if seepage is under saturated 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 adequate to erode materials and lead to piping and structural failure [9,14].

When and Where Should Seepage Samples be Collected?

Any dam or embankment showing changes in seepage patterns over time, or sited on limestones, breccias, and other porous rock formations with evidence of gypsum, anhydrite, calcite, dolomite, or other 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, that applies a standard methodology to identify existing dams that might be at structural risk from mineral dissolution and other issues. The CFR report will sometimes recommend 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 post-construction seepage chemistry programs should be collected 1 -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 post-repair 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! Observation of new seeps, spreading of a seepage outflow, increased or unusual flows, cloudy flows containing suspended particles, and slumping, cracking, or progressive changes in structural features are direct indicators that alert project managers to potential seepage problems and the need for seepage sample collection and closer flow and piezometer monitoring.

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 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 will also be similar. When seepage flow increases for the same historical reservoir elevations, then seepage is increasing and flow paths are widening.

To summarize, seepage samples should be collected and analyzed under the following circumstances:

1. When a dam is sited on rock formations susceptible to mineral dissolution and has developed seepage problems, or when the Dam Safety CFR recommends seepage testing.
2. After first filling or post-repair 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.
3. Whenever physical site inspection reveals unexpected changes in seepage or structural behavior.
4. 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. Example sample submittal forms and sources for field equipment and services are summarized elsewhere [1]. Use the following general rules to choose collection stations:

1. 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 multi probe.
2. Collect surface seepage as close as possible to the dam. As you move farther downstream, there is a greater likelihood 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, routine collection is not advised.
3. Collect samples from established seeps at the weir, and only when flow is measurable. If there is water 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.
4. Collect samples from new seeps and sand boils at the emergence point.
5. Collect well and piezometer samples only from tubes and wells that intersect the rock formation of concern. Collect samples only from active piezometers that are being currently read. Independently measure depth to water surface before sampling piezometers and wells.
6. Always collect samples from wells that become artesian.

Interpreting Seepage Chemistry and Dissolution

This section will address some basic concepts about how to interpret chemistry data from reservoir, seeps, and wells at a dam where seepage is a concern. The primary approach for interpreting seepage chemistry data is as follows:

1. Plotting the data 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.
2. Calculating *mineral saturation indices* for each sample using a computer chemical equilibrium program such as WATEQ4F [54,55], MINTEQA2 [56], or PHREEQE [57], and examining differences between reservoir and seepage.
3. 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.
4. Determining the effect of mixing on the observed concentration differences by applying mixing models, such as NETPATH [44] or stable isotope investigations [58].
5. Development of a geochemical mass balance model to help account for difference data not attributable to mixing.
6. 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, difference diagrams, and other multivariate plotting techniques. Plotting the data should be considered the first step in any seepage chemistry interpretation process.

One of the best ways to use polygon plots is to group seepage and well plots with reservoir water plots, as seen in figure 3a, which shows Stiff diagrams plotted for seepage and reservoir data from Horsetooth Dam, Colorado-Big Thompson Project, Ft. Collins, Colorado. The left-hand diagrams are a comparison of averaged historical data collected from wells intercepting specific geological strata with average reservoir concentrations. The right-hand Stiff diagrams plot trace elements Si, Fe, Mn, and Al, along with the major ions. Note that the trace elements have been entered as mg/L while the major ions are entered as meq/L, allowing a comparison of both sets of data. Figure 3b shows Stiff diagrams plotted on a plan map. This approach, along with annotating geologic cross section drawings with Stiff diagrams is a good method to associate chemistry with specific strata and structural features. Public domain software is also available to plot Stiff diagrams on geographic information system maps [59].

Mineral Saturation Index Calculations using Computer Models

Computer chemical equilibrium programs such as MINTEQA2 [56], and PHREEQE [57] 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 what are called mineral saturation indices (SI's) - one of the most useful output parameters for seepage evaluations. Craft [1] provides a standard operating procedure for entering data and running the MINTEQA2 model.

Saturation Indices - The SI is denoted as "Log AP/KT" in both model's output tables. MINTEQA2 evaluates chemical concentration data and calculates saturation indices for

minerals potentially responsible for the particular sample's chemical concentrations. Basically, the saturation index 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 over saturated 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 under saturated with respect to calcite. These waters will tend to *dissolve* calcite.

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.

MINTEQA2 Assumptions and Limitations - While the MINTEQA2 model will calculate a wealth of output, there are several important assumptions required for accurate output estimates. These are discussed more fully by Craft [1].

Difference Data and Mass Balance Models

This section describes the approach used to estimate mass wasting and void formation rates along seepage paths.

Difference Data - Difference data (denoted as Δ_i - where i represents the measured chemical constituent), are 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 transit for a given constituent that could be caused by dissolution or bacterial processes. Negative values suggest a net loss for a given constituent that could be due to precipitation, bacterial respiration, or cation exchange. In the context of the mass balance model, these concentration changes provide the clues suggesting that certain chemical processes are occurring during seepage transit. Table 3 provides a summary of the processes that may account for changes in seepage concentrations.

Developing a Mass Balance Model - Before we can calculate mass wasting and void formation associated with mineral dissolution, we need to develop what is called a *mass balance model.* Mass balance models are a set of processes and chemical reactions thought to produce the changes observed in seepage chemistry that are consistent with available petrographic and other evidence. While a good mass balance model can be semi-quantitative in accounting for changes in seepage chemistry, it's application is not simple. The general approach suggested by [23,60,61,62] 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 [19,20,23,31,36].

Mixing and Other Processes - Mixing or dilution can also be included as a component process in a mass balance model, and computer models like NETPATH [44] may used to evaluate whether chemical changes between reservoir and seepage may be caused by mixing

Figure 3a - 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.
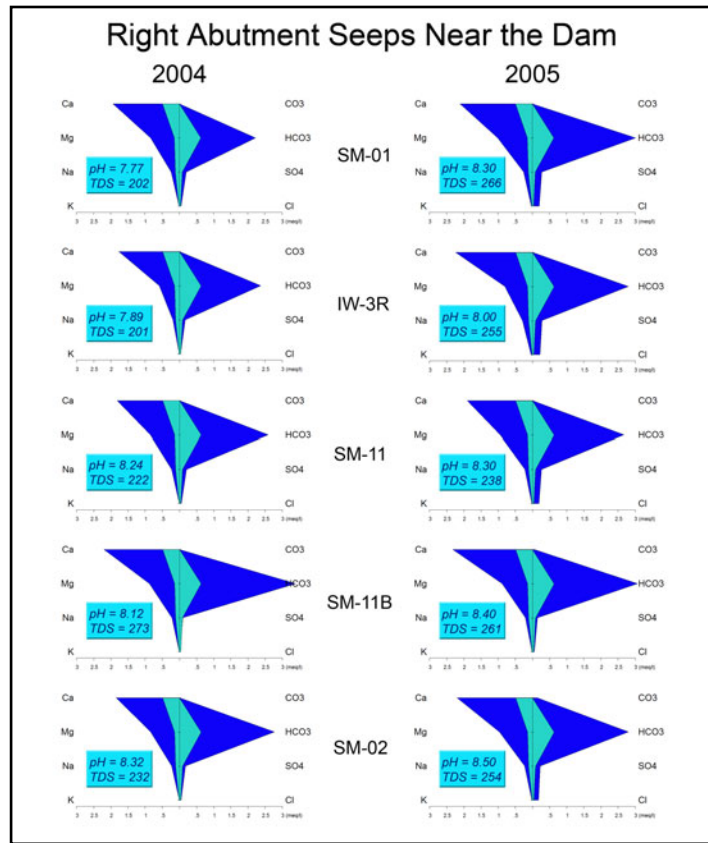

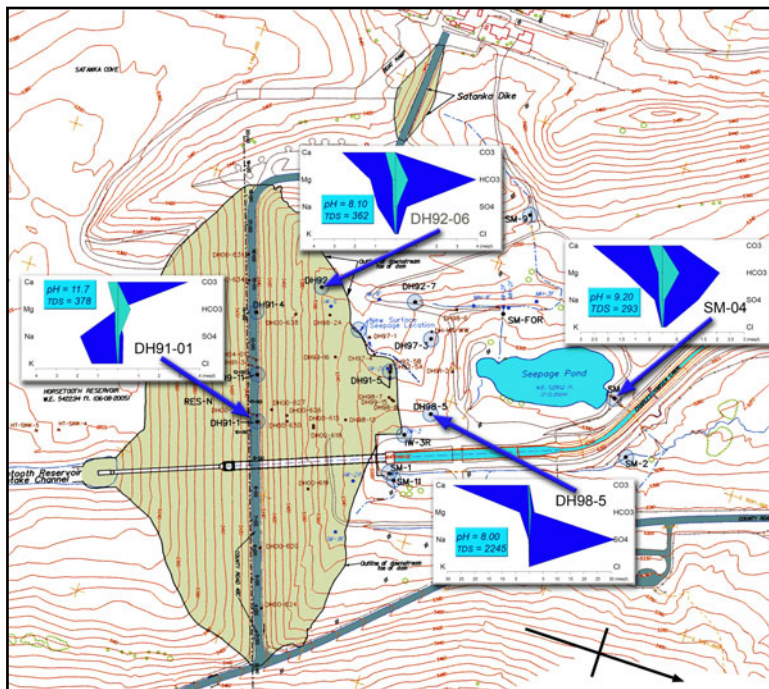Figure 3b - Stiff diagrams showing seepage and reservoir chemistry plotted on a plan map.

Table 3 - 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 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

of reservoir water with another groundwater - perhaps a pre-impoundment 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 pre-impoundment aquifer- the *end member* sample data [40]. This information is not always available, and drilling and well development may be required to obtain it.

Developing a Set of Calculation Rules - Next, as set of calculation rules are developed for the proposed reactions and possible mixing processes where difference data for constituents having a unique cause and associated reaction, such as loss of Na^+ from cation exchange, are calculated prior to data having several possible causes and associated chemical reactions.   The coefficients used in the calculation rules are obtained directly from the balanced chemical reactions thought to account for the difference data. An example of a set of calculation rules can be found in Craft [1]. Table 4 is a summary of mass balance results at Deer Flat Embankments, Boise Project, Idaho, where the dominant processes are summarized for the Deer Flat Embankments seepage study [34]. This is a good example that demonstrates how a mass balance model suggests that many changes in seepage concentration are not caused by mineral dissolution. Often a much simpler conceptual model (for example, gypsum, calcite and biotic processes only) can be applied to get the same general results as suggested by Craft and Pearson [64].

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 [65]. Detailed example calculations are provided by Craft [1].

Computer Groundwater Flow Models - Tools such as the MODFLOW model [49] are valuable for determining likely seepage flow patterns, seepage residence times in 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 [66]. Often, changes in seepage chemistry are directly dependent on hydrologic factors. The MODFLOW model was applied during a seepage investigation at Glen Canyon Dam [26] 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.

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 makes 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 skills in analytical chemistry, hydrology, geophysics, structural geology, petrography, and civil engineering.

Table 4 - 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 [34].

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	0.100
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

The Sampling Plan

A sampling plan should be developed by a chemist in consultation with project geologists, hydrologists, engineers and field personnel. This sampling plan is an important organizing tool and can be adapted with minor formatting to provide instructions and guidance to field offices. Discussing the problem and developing such a plan will ensure that *meaningful information* is obtained from chemical data and that the important questions are answered. This process will also avoid selection of redundant or ambiguous sampling sites or wasting resources on overly frequent sampling. The following issues (discussed more fully in [1]) should be addressed by the sampling plan:

1. Definition of the Problem
2. Review of Pertinent Background Data
3. Selection of Seepage Water Sampling Sites and Chemical Tests
4. Identify Additional Samples/Tests
5. Quality Control for Chemical Analyses
6. Data Analysis and Interpretation of Data

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:

1. Mandatory - Water samples from the Reservoir for chemical analyses
2. Mandatory - Water Samples from Active Seeps for chemical analyses
3. Mandatory (if available) - Water samples from observation wells in abutments, foundation, or embankment
4. Mandatory (if available) - Water samples from structural drains and galleries for chemical analyses
5. Mandatory (if available) - Solid samples of any precipitates or deposits near seepage emergence points
6. Mandatory (if present in seepage water) - Solid samples of materials suspended in seepage flows - separated by filtration for petrographic tests.
7. Water Samples from Pre-Impoundment or "Native" Groundwater (if available) for chemical analyses
8. Solid Samples from Borrow Areas for petrographic examination and leaching tests
9. Solid Samples from embankment, abutments, and foundation for petrographic examination and/or leaching tests

Water Samples to Avoid -   Avoid water samples from surface ponds and catchments that collect seepage from several sources and are subject to surface run-off 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.

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 2-3 days, and to consistently sample the same sites over time. Nomenclature for piezometers, wells and seeps often vary between designers, area office personnel, and irrigation districts. A single set of station identifiers should be used. These precautions assure 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. When possible, measure or note the following at the time of sampling:

1. Date, time, air temperature, general weather conditions.
2. Reservoir Elevation.
3. Seepage Flow Rate or piezometer level prior to pumping or sampling.
4. Seepage and Reservoir Sample temperature, to $\pm$ 0.2°C.
5. pH and Alkalinity (unless lab can analyze within 24 hr).
6. DO using a modified Winkler titration, or a calibrated DO probe.
7. Presence of any notable odor at the sampling site, especially hydrogen sulfide (rotten egg) odor.

8. Presence and photographs of any mineral deposits in or around the seepage sampling site.
9. Any indication of piping or excessive suspended materials in seepage water.
10. Any other field observations pertinent to the problem.
11. 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: Craft [1] 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:

1. Major Ions, including Sodium, Potassium, Calcium, Magnesium, Sulfate, Chloride, Carbonate, and Bicarbonate.
2. Lab pH, Conductivity, and Filterable Residue (180 C).
3. Trace Metals: Iron, Manganese, and Aluminum.
4. Silica as SiO_2 (may also be analyzed as a trace metal).
5. 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.

We recommend that seepage chemistry team members obtain access to a copy of *Standard Methods for the Examination of Water and Wastewater* [27]. 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* [67], which provides cross reference tables for EPA [68,69] and *Standard Methods* [27] chemical analysis 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 validation, and final purpose and intended use of results [70]. QA includes problem definition, sample site selection, frequency of sampling, sampling procedures, chemical analysis quality, as well as final data 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. More details regarding QA for studies involving analytical chemistry are covered elsewhere [1,70,71,72,73].

Procedures for Collecting Seepage Water Samples
Detailed procedures to collect and preserve seepage and other water samples for chemical analyses during dam safety investigations are summarized elsewhere [1,74,75,76,77].

Conclusions

Dam seepage investigations where structures, foundations, and abutments contain soluble minerals such as limestone, gypsum, or anhydrite, can benefit from interdisciplinary efforts that include the active participation of chemists, geologists, and hydrologists, along with engineers. When comparing the chemistry of reservoir and seepage, accurate and properly collected water chemistry data can be used to better understand the rate of void formation and the nature of mineral dissolution. This is important information that can be helpful assessing the severity and progression of the seepage problem. However, the proper use of consensus standards for sample collection and quality assurance for chemical testing, and the skilled

application of geochemical tools such as mass balance models and computer chemical equilibrium models are essential to high quality interpretative information concerning mineral dissolution and seepage.

Acknowledgments

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