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Managing Water in the West

Water Chemistry Analysis for Water Conveyance, Storage, and Desalination Projects

Manuals and Standards Program

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Contents

Executive Summary

Understanding the chemical and physical properties of water being conveyed, stored or treated is essential for designing systems or appurtenant equipment. This document presents a spreadsheet tool that can be used to analyze the chemical composition of a water source. Basic principles of water chemistry that are necessary to make use of the spreadsheet are included.

The Chemical Analysis Spreadsheet is used for the following:
- To identify whether the water analysis is satisfactory in terms of ion balance
- To indicate the probability of aggressive attack of water on adjacent metal surfaces **or** the generation of scaling layers on adjacent surfaces
- To characterize the likelihood of scale formation from sparingly soluble salts
- To calculate the values of the most commonly used calcium carbonate scaling potential indices

The results of the spreadsheet can be used to:

a) identify whether new or additional water quality analysis should be conducted; and

b) determine whether pH adjustment or anti-scalant addition is needed to reduce the likelihood of scaling or corrosion of pipes and equipment.

This publication serves as a users' manual for the spreadsheet and is organized into the following sections:
- Overview and presentation of the spreadsheet
- Spreadsheet input parameters
- Major ion analysis
- Saturation calculations for sparingly soluble salts
- Calculation of commonly used scaling potential indices, and
- Interpretation of results from calculations

The Chemical Analysis Spreadsheet

The Chemical Analysis Spreadsheet, shown in Figure 1, was designed as a screening tool that requires relatively few inputs and provides a quick assessment of standard water quality parameters and sparingly soluble salt scaling potential. The spreadsheet can be accessed through the Bureau of Reclamation website at http://www.usbr.gov/pmts/water/publications/wqspreadsheet.html.

Chemical Analysis Work Sheet for:			Sample source			
			Sample identification			
FEED WATER COMPOSITION:						
Na^+	93.00	mg/L =	4.05	meq/L =	0.00405	m/kg water
K^+	9.00	mg/L =	0.23	meq/L =	0.00023	m/kg water
Ca^{2+}	196.30	mg/L =	9.80	meq/L =	0.00491	m/kg water
Mg^{2+}	120.40	mg/L =	9.90	meq/L =	0.00496	m/kg water
Ba^{2+}	142.60	ug/L =	0.002	meq/L =	0.00000	m/kg water
Sr^{2+}	120.00	ug/L =	0.003	meq/L =	0.00000	m/kg water
Sum of Cations			23.98	meq/L		
Cl^-	1.90	mg/L =	0.05	meq/L =	0.00005	m/kg water
F^-	0.50	mg/L =	0.03	meq/L =	0.00003	m/kg water
HCO_3^-	169.20	mg/L =	2.77	meq/L =	0.00278	m/kg water
SO_4^{2-}	953.00	mg/L =	19.84	meq/L =	0.00994	m/kg water
NO_3^-	10.00	mg/L =	0.16	meq/L =	0.00016	m/kg water
Sum of Anions			22.86	meq/L		
Cation/Anion Difference		2.401%	Balance is	acceptable.		
Silica	13.00	mg/L				
Sum of Ions	1553.56	mg/L				
TDS by calc.	1566.56	mg/L				
TDS by evap.	1463.00	mg/L				
pH	7.50					
Temp.	15.00	deg. C =	59.00	deg. F		
Ionic Strength:	0.0433	m/kg water				
Ksp $CaSO_4$:	1.80E-04	IP $CaSO_4$:	4.86E-05		IP/Ksp:	0.27
Ksp $BaSO_4$:	4.92E-10	IP $BaSO_4$:	1.03E-08		IP/Ksp:	20.94
Ksp $SrSO_4$:	1.18E-06	IP $SrSO_4$:	1.36E-08		IP/Ksp:	0.01
IP CaF_2 max:	4.00E-11	IP CaF_2:	3.39E-12		IP/IP max	0.08
Langelier Saturation Index						0.18
Ryznar Index						7.14
Stiff and Davis Index						0.12
Larson-Skold Index						7.17
Notes:						
To use this sheet, replace red items with appropriate data.						
If concentration is unknown, insert 0. If temperature is unknown, insert 20.						
If TDS by evaporation has been measured, it can be compared to the calculated TDS.						

Figure 1. Chemical analysis spreadsheet.

Spreadsheet Inputs

Spreadsheet cells are provided for identification of the water source and other specific information about the particular sample.

The main inputs to the chemical analysis spreadsheet are concentrations, in milligrams per liter (mg/L[1] or micrograms per liter (µg/L), of the major ions in the feed water. Required inputs are denoted in red text within the spreadsheet.

The following are cation concentration inputs:
- Sodium (Na^+), mg/L
- Potassium (K^+), mg/L
- Calcium (Ca^{2+}), mg/L
- Magnesium (Mg^{2+}), mg/L
- Barium (Ba^{2+}), µg/L
- Strontium (Sr^2+), µg/L

The following are anion concentration inputs:
- Chloride (Cl^-), mg/L
- Fluoride (F^-), mg/L
- Bicarbonate (HCO_3^-), mg/L
- Sulfate (SO_4^{2-}), mg/L
- Nitrate (NO_3^-), mg/L

The following are other laboratory-derived components or water property inputs:
- Silica concentration, mg/L
- pH, dimensionless
- Total Dissolved Solids (TDS), mg/L (optional)
- Temperature, degrees Celsius

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[1] The frequently used expressions of concentration milligrams per liter and parts per million (by weight) are not the same. But for a majority of compositions and temperatures that will be encountered, the specific gravity of water is sufficiently close to 1.0 that these concentrations are numerically very similar. However, with seawater and its concentrates, the difference is a few percent or more.

Spreadsheet Outputs

The following are outputs of the water analysis spreadsheet:

Major ion analysis
- Sum of anions
- Sum of cations
- Cation/anion difference
- Overall accuracy of ion analysis
- Calculated TDS
- Ionic strength

Evaluation of precipitation potential of sparingly soluble salts
- Solubility product constant (K_{sp}) of $CaSO_4$
- K_{sp} of $BaSO_4$
- K_{sp} of $SrSO_4$
- Maximum ion product (IP_{max}) for CaF_2
- Ratio of ion product to K_{sp} for $CaSO_4$
- Ratio of ion product to K_{sp} for $BaSO_4$
- Ratio of ion product to K_{sp} for $SrSO_4$
- Ratio of ion product to maximum ion product for CaF_2

The values of the following indices relating to calcium carbonate scaling:
- Langelier Saturation Index (LSI)
- Stiff and Davis Stability Index (S&DSI)
- Ryznar stability index
- Larson-Skold Index (L&SkI)

The following sections describe the calculations that were used in the spreadsheet and the water chemistry principles supporting those calculations.

Major Ion Analysis

Total dissolved solids (TDS), electrical conductivity, and ionic strength are the three parameters used to describe the total solute concentration in a water sample. These parameters do not discriminate between the types of solutes in solution; they give a measure of the overall concentration of constituents.

Total Dissolved Solids

The total dissolved solids concentration is typically determined by heating a filtered sample of water at a temperature slightly above 100 °C until only a dry residue remains. During the drying step, the dissolved gases (primarily oxygen, nitrogen, and carbon dioxide) are vaporized. The dissolved ions, neutral inorganic molecules, and neutral organic molecules remain in the residue. In most natural water sources, the majority of the dry residue is comprised of inorganic salts; therefore, the TDS can be considered a measure of the ionic content of the water (Benjamin 2002).

Ionic Strength

The ionic strength of water takes into account the impact of the ionic charge of a species on chemical interaction in solution. Ionic strength, I, is calculated using Equation 1.

$$I = \frac{1}{2}\sum_{\text{all ions}} c_i Z_i^2$$
<div align="right">Equation 1.</div>

where c_i is the concentration of species i (mol/L), and Z_i is the charge of the species, i; Z is considered dimensionless, so I has units of mol/L.

The spreadsheet converts constituent concentrations in mg/L to milli-equivalent concentrations (MEQ) by Equation 2.

$$MEQ\left(\frac{meq}{L}\right) = \frac{C\left(\frac{mg}{L}\right)}{molar\ mass\left(\frac{mg}{mmol}\right)} * valence\left(\frac{eq}{mol}\ or\ \frac{meq}{mmol}\right)$$
<div align="right">Equation 2.</div>

The spreadsheet evaluates the suitability of the water analysis by checking the balance between anions and cations. The tests for major cations and anions are performed separately, and each test includes a certain degree of error. The anion/cation balance, which should always be performed on a chemical analysis of water, quantifies the reliability of the data. The percent difference between sum of the milli-equivalents of cations and anions is calculated using Equation 3.

$$\frac{\sum cations\left(\frac{meq}{L}\right)-\sum anions\left(\frac{meq}{L}\right)}{\sum cations\left(\frac{meq}{L}\right)+\sum anions\left(\frac{meq}{L}\right)}*\cdot \mathbf{100}\%$$

Equation 3.

If the difference between the cation and anion concentrations is less than 5 percent, the water analysis is considered adequate (Standard Methods, 19th Ed., 1995, p. 1-12). Based on the experience of the spreadsheet developer, Frank Leitz, the following additional qualifications are considered for the sum of ions:
- If the sum is between 5 and 10 percent, it is questionable, but still usable, and
- A difference of greater than 10 percent is considered poor. If the water balance is poor, the water source should be resampled and reanalyzed.

The sum of ions is computed as the sum of the concentration in mg/L of the cations and the anions. The calculated TDS is equal to the sum of the ions plus the concentration of silica.

Degree of Saturation of Sparingly Soluble Salts

The chemical composition of water determines the stability of the water or the likelihood of precipitation of sparingly soluble salts or the tendency to cause corrosion by scavenging minerals from surrounding materials such as tanks and pipes. The spreadsheet computes the solubility products for calcium sulfate ($CaSO_4$), barium sulfate ($BaSO_4$), and strontium sulfate ($SrSO_4$), and the ion product for calcium fluoride (CaF_2).

The solubility product, K_{sp}, is the equilibrium constant for a chemical reaction which a solid ionic compound dissolves to yield ions in solution. When the product of the molar concentrations of the salt ions in solution are equal to K_{sp}, the solution is considered to be 100-percent saturated. Further addition of ions is expected to result in precipitation of the sparingly soluble salt. The K_{sp} is a function of the ionic strength and temperature of the water sample.

The solubility products for sparingly soluble salts are based on expressions derived from published data on solubility as a function of the ionic strength of the solution at a given temperature. Equations 4–6 are expressions for calculating K_{sp} for $CaSO_4$, $BaSO_4$, and $SrSO_4$ at 25 °C (Dupont 1992).

$$K_{sp}CaSO_4 = 10^\wedge \left(\frac{1}{-0.022((\log(IS)+2.2954^2)-0.2478)} \right) \qquad \text{Equation 4.}$$

$$K_{sp}BaSO_4 = 10^\wedge \left(\frac{1}{-0.0026((\log(IS)+2.8747^2)-0.1015)} \right) \qquad \text{Equation 5.}$$

$$K_{sp}SrSO_4 = 10^\wedge \left(\frac{1}{-0.0079((\log(IS)+2.8154^2)-0.152)} \right) \qquad \text{Equation 6.}$$

Consider an ionic solution consisting of calcium and sulfate. The following equation describes the equilibrium between solid calcium sulfate and its ions:

$$CaSO_4(s) \overset{eq}{\leftrightarrow} Ca^{2+}(aq) + SO_4{}^{2-}(aq) \qquad \text{Equation 7.}$$
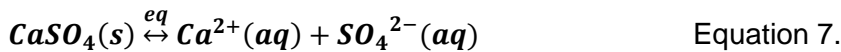
The ion product (IP) for a desired salt is calculated using the molar concentrations of the constituents in water. So, for calcium sulfate, the IP is the product of the molar concentration of calcium and sulfate, Equation 8. If the ion product is greater than the solubility product, or the value of the IP divided by the solubility product is greater than one, precipitation is expected to occur.

$$IP = [Ca^{2+}][SO_4^{2-}] \qquad \text{Equation 8.}$$

Scale formation by calcium fluoride (CaF_2) is considerably less likely than scaling by the compounds discussed above. Perhaps because of this reason, data on the solubility of calcium fluoride is less widely available.

Indices for Predicting Calcium Carbonate Scaling Potential

Scaling potential indices have been developed to predict the likelihood of calcium carbonate precipitation. These indices are convenient, easy to use, and provide a reasonable estimate of the likelihood of scaling in water sources. The most widely used indices in the water treatment industry are the Langelier Saturation Index (LSI), Stiff and Davis Stability Index (S&DSI), the Ryznar stability index, and the Larson-Skold Index. The Calcium Carbonate Precipitation Potential (CCPP) is preferred by some but is considerably more complicated to calculate. Other less frequently used indices include the Puckorius scaling index and the Oddo-Tomson index.

Scaling potential indices are only capable of predicting the potential or propensity of a water to form scale. Analysis of a water source may indicate the propensity to form scale, based on the value of the scaling index, and may not actually produce precipitate due to one or more of the following:

1. The kinetics of the reaction might be too slow,
2. The induction period for formation of the precipitate may be longer than the residence time in the system.
3. A low buffering capacity may affect the capacity of the water to hold precipitate.

These indices are conservative estimates for determining the recovery limits in desalination units and do not take into account the kinetics of the precipitation reaction or the induction time required for precipitate to form, both of which are affected by the hydrodynamics of the system (Sheikholeslami 2003).

The presence of a thin layer of scale is usually beneficial for prevention of corrosion of metallic piping. For maximum benefit, one needs neither too much nor too little scale deposition. The Langelier index was initially developed to quantify this operation.

The following sections describe the spreadsheet calculations for computing the LSI, S&DSI, Ryznar, and Larson-Skold Indices for calcium carbonate precipitation potential. Guidelines are provided for how to interpret the values of the calculated indices.

Langelier Saturation Index

The LSI is used to determine the need for calcium carbonate precipitation scale control in water sources containing a TDS concentration of less than 10,000 mg/L (ASTM 1998). The following calculations are used to compute the LSI:

1. Compute the value of "pCa," defined as the negative logarithm of the molar calcium concentration.
2. Compute the value of "pAlk," defined as the negative logarithm of the molar bicarbonate concentration.
3. Obtain "C" as a function of the TDS concentration (mg/L) and the temperature (°F) by curve fitting to the LSI chart, which results in Equation 9. While this chart is available from a number of references, the chart in DuPont (1992) was used to obtain Equation 9.

$$C(TDS, T) = 3.26e^{-0.005 \cdot T} - 0.0116 \log_{10}(TDS^3) + 0.0905 \log_{10}(TDS^2) - 0.133 \log_{10}(TDS) - 0.02$$

Equation 9.

T is in °F.

4. The saturation pH is then calculated by Equation 10.

$$pH_{sat} = pCa + pAlk + "C"$$

Equation 10.

5. Equation 11 is used to determine the value of the LSI:

$$LSI = pH - pH_{sat}$$

Equation 11.

Water with an LSI value more negative than –0.5 is described as "aggressive." An aggressive water will not deposit a protective film or layer of calcium carbonate, which a water with a positive LSI would do. Instead it will dissolve such a film where one exists. This leaves any exposed metallic surfaces unprotected and open to corrosion resulting from phenomena like galvanic differences, low pH, or significant concentrations of sulfate or chloride ions.

An aggressive water will also attack concrete. This means that concrete lining pipe may not be a satisfactory means of protecting metallic pipe.

Two different sets of criteria used for interpreting the value of the LSI are described in Tables 1 and 2.

Table 1. Interpretation of LSI Values (Tchobanoglous, Burton et al. 2003).

LSI value	Interpretation
LSI < 0	Water is undersaturated with respect to calcium carbonate. Undersaturated water has a tendency to remove existing calcium carbonate protective coatings in pipelines and equipment.
LSI = 0	Water is considered to be neutral. Neither scale-forming nor scale removing.
LSI > 0	Water is supersaturated with respect to calcium carbonate ($CaCO_3$), and scale formation may occur.

Table 2. Alternative Interpretation of LSI Values (Carrier Air Conditioning Company 1965)

LSI value	Interpretation
2.0	Scale forming, but non-corrosive
0.5	Slightly scale forming and corrosive
0	Balanced, but pitting corrosion possible
-0.5	Slightly corrosive, but not scale forming
-2.0	Serious corrosion

Adjustment of LSI

If the LSI of the water sample is unacceptable, adjustments can be made by changing the water chemistry. The two ways of accomplishing this, described in ASTM D3739, are to decrease the calcium concentration in the water or to add acid to lower the pH.

Reducing the calcium concentration in the feed can be accomplished by softening or ion exchange processes. Decreasing the calcium concentration will lower the pCa, which will in turn decrease the LSI. Softening will not change the alkalinity or pH of the feed solution, and the slight change in TDS will be negligible. After calcium concentration adjustment, the LSI can be recalculated using the procedure described in the previous section (ASTM D3739 2010).

Adding acid, such as hydrochloric acid (HCl), carbon dioxide (CO_2), or sulfuric acid (H_2SO_4), changes the Alk, C, and pH. The change is TDS is considered to be negligible. Adding acid will lower the LSI. However, since acidification also affects other parameters, trial and error computations are recommended to find the appropriate acid dose to obtain the desired LSI (ASTM D3739 2010).

To use the spreadsheet to identify the effects of acid addition on LSI, select the type of acid to be used and a dose rate. Calculate the new values of pAlk and pC after acid addition using the raw water values and the concentration of acid using the following equations:

For H_2SO_4 addition, where $x = $ mg/L (100% H_2SO_4):

$$Alk(acid) = Alk - 1.02 \cdot x$$
$$C(acid) = C + 0.9 \cdot x$$

For HCl addition, where $y = $ mg/L (100% HCl):

$$Alk(acid) = Alk - 1.37 \cdot y$$
$$C(acid) = C + 1.21 \cdot y$$

Next, calculate the ratio Alk/C(acid). Using equation 12 derived from ASTM D3739, calculate pH(acid).

$$pH = 0.4275 \cdot ln\left(\frac{Alk}{co}\right) + 6.3066 \qquad \text{Equation 12.}$$

Next, calculate the new value of pH_{sat} using equation 10, and the value of LSI after acid addition using equation 11. Continue to adjust the concentration of acid added to obtain the desired value of LSI.

Figure 2 depicts the spreadsheet that is used to calculate the effects of acid addition on LSI.

Acid addition LSI Adjustment for:	**Sample source**
	Sample identification
Type of acid used	HCl
Acid added, mg/L	0.05
pAlk (raw water)	2.56
pC (raw water)	2.45
pAlk(acid)	2.51
pC(acid)	2.50
ratio (Alk/CO2)	1.00
pH(acid)	6.31
pHs(acid)	7.31
Adjusted LSI	**-1.01**
To use this sheet, select the type of acid to be used and specify the acid dose.	

Figure 2. LSI adjustment with acid addition.

Stiff and Davis Stability Index

The Stiff and Davis Saturation Index (S&DSI) is used to predict calcium carbonate scaling potential. This method is most appropriate for water sources containing more than 10,000 mg/L of total dissolved solids (ASTM 1996). The following is the procedure used to calculate the value of the S&DSI:

1. Calculate the "K" value using the following curve-fitting equation developed from the figures presented in ASTM Standard 4582

If I < 1.2,

$$K = 2.022e^{\frac{(\ln I + 7.544)^2}{102.60}} - 0.0002T^2 + 0.00097T + 0.262$$

Equation 13.

If I > 1.2,

$$K = -0.1I - 0.0002T^2 - 0.00097T + 3.887$$

Equation 14.

2. Calculate the saturation pH using the following equation using the values of pCa and pAlk calculated for the LSI:
$$pH_{sat} = pCa + pAlk + K$$

3. Calculate the value of the S&DSI by the following:
$$S\&DSI = pH - pH_{sat}$$

A positive value of S&DSI indicates the tendency to form a calcium carbonate scale (ASTM 1996).

Ryznar Index

The Ryznar Index (RI) is an alternative method to the LSI for computing calcium carbonate scale formation. The RI is given by the following expression:

$$RI = 2 \cdot pH_{sat} - pH$$

This is directly related to the LSI by:

$$RI = pH - 2 \cdot LSI$$

This value is computed using the pH of the water sample and the saturation pH, pH_{sat}, as determined for the calculation of the LSI.

The criteria for interpreting the value of RI are as follows (Tchobanoglous, Burton et al. 2003):

RI Value	Significance
RI < 5.5	Heavy scale likely to form
5.5 < RI < 6.2	Moderate scale formation likely
6.2 < RI < 6.8	Water is considered neutral
6.8 < RI < 8.5	Water is aggressive and corrosion is likely
RI > 8.5	Water is considered very aggressive, and substantial corrosion is possible

Larson-Skold Index

The Larson-Skold Index (L&SkI) is used to describe the corrosivity of water towards mild steel and was developed based on in-situ measurements of corrosion in steel lines transporting Great Lakes water (Larson and Skold 1958). The index describes the ratio of concentration of chloride and sulfate ions to the concentration of bicarbonate and carbonate ions. Because the L&SkI is an empirical correlation, its utility for describing corrosion for other types of water is questionable. The following equation is used to calculate the S&SI:

$$L\&SkI = \frac{(Cl^- + SO_4^{2-})}{(HCO_3^- + CO_3^{2-})}$$

The ion concentrations are expressed in equivalents per million. The following table describes the criteria for evaluating values of L&SkI (Larson and Skold 1958).

L&SkI Value	Significance
< 0.8	Chloride and sulfate concentrations will not interfere with natural film formation
0.8 < L&SkI < 1.2	Chloride and sulfate concentrations may interfere with natural film formation; corrosion may occur
> 1.2	High corrosion rates are anticipated

Interpreting the Values of the Scaling Indices

While each of the scaling indices calculated in the spreadsheet assesses the likelihood of scaling or corrosion based on calcium carbonate chemistry, each index is based on slightly different principles. Therefore, the computed value of each index should be considered when analyzing a water sample. Additionally, the user of this spreadsheet should be aware that the index values are only approximations and that the actual behavior of the water may vary based on the site-specific conditions or other water quality parameters not considered in the calculation of the index.

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