Designation: D4692 – 01 (Reapproved 2010)

Standard Practice for
Calculation and Adjustment of Sulfate Scaling Salts ($CaSO_4$, $SrSO_4$, and $BaSO_4$) for Reverse Osmosis and Nanofiltration[1]

This standard is issued under the fixed designation D4692; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers the calculation and adjustment of calcium, strontium, and barium sulfates for the concentrate stream of a reverse osmosis or nanofiltration system. The calculations are used to determine the need for scale control in the operation and design of reverse osmosis and nanofiltration installations. This practice is applicable for all types of reverse osmosis devices (tubular, spiral wound, and hollow fiber) and nanofiltration devices.

1.2 This practice is applicable to both brackish waters and seawaters.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D511 Test Methods for Calcium and Magnesium In Water
D516 Test Method for Sulfate Ion in Water
D1129 Terminology Relating to Water
D3352 Test Method for Strontium Ion in Brackish Water, Seawater, and Brines
D4194 Test Methods for Operating Characteristics of Reverse Osmosis and Nanofiltration Devices
D4195 Guide for Water Analysis for Reverse Osmosis and Nanofiltration Application
D4382 Test Method for Barium in Water, Atomic Absorption Spectrophotometry, Graphite Furnace
D6161 Terminology Used for Microfiltration, Ultrafiltration, Nanofiltration and Reverse Osmosis Membrane Processes

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology D1129 and D6161.

3.2 *Definitions of Terms Specific to This Standard*—For definitions of terms relating to reverse osmosis, refer to Test Methods D4194.

4. Summary of Practice

4.1 This practice consists of calculating the potential for scaling by $CaSO_4$, $SrSO_4$, and $BaSO_4$ in a reverse osmosis or nanofiltration concentrate stream from the concentration of Ca^{++}, Sr^{++}, Ba^{++}, and $SO_4^=$ in the feed solution and the recovery of the reverse osmosis or nanofiltration system.

4.2 This practice also presents techniques to eliminate scaling by decreasing the recovery, by decreasing the Ca^{++}, Sr^{++}, and Ba^{++} concentrations in the feed water, and by addition of scale inhibitors.

5. Significance and Use

5.1 In the design and operation of reverse osmosis and nanofiltration installations, it is important to predict the $CaSO_4$, $SrSO_4$, and $BaSO_4$ scaling properties of the concentrate stream. Because of the increase in total dissolved solids and the increase in concentration of the scaling salts, the scaling properties of the concentrate stream will be quite different from those of the feed solution. This practice permits the calculation of the scaling potential for the concentrate stream from the feed water analyses and the reverse osmosis or nanofiltration operating parameters.

5.2 Scaling by $CaSO_4$, $SrSO_4$, and $BaSO_4$ will adversely affect the reverse osmosis or nanofiltration performance. This practice gives various procedures for the prevention of scaling.

6. Procedure

6.1 Determine the concentrations of Ca^{++}, Sr^{++}, Ba^{++}, and $SO_4^=$ in the feed stream in accordance with Test Methods D511, D3352, D4382, and D516, respectively.

NOTE 1—If H_2SO_4 is used for control of $CaCO_3$ scale, measure the $SO_4^=$ after acid addition.

6.2 Determine the concentration of all major ions using the appropriate methods given in Guide D4195. At a minimum, the

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[1] This practice is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.08 on Membranes and Ion Exchange Materials.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

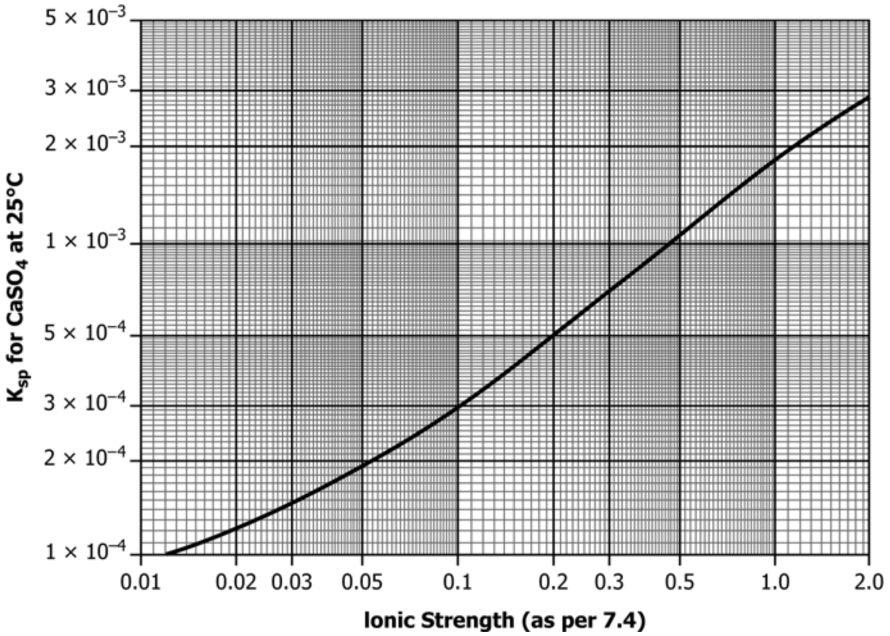

FIG. 1 K_{sp} for $CaSO_4$ versus Ionic Strength

concentrations of Mg^{++}, Na^{+}, HCO_3^{-}, and Cl^{-} must be determined.

7. Calculation

7.1 Calculate the calcium concentration in the concentrate stream from the calcium concentration in the feed solution, from the recovery of the reverse osmosis or nanofiltration system, and from the calcium ion passage as follows:

$$Ca_c = Ca_f \times \frac{1 - Y\left(SP_{Ca}\right)}{1 - Y}$$

where:

Ca_c = calcium ion concentration in concentrate, mg/L,
Ca_f = calcium ion concentration in feed, mg/L,
Y = recovery of the reverse osmosis system, expressed as a decimal, and
SP_{Ca} = calcium ion passage, expressed as a decimal.

NOTE 2—SP_{Ca} can be obtained from the supplier of the reverse osmosis or nanofiltration system. For most reverse osmosis and nanofiltration devices, SP_{Ca} can be considered to be zero, in which case the equation simplifies to:

$$Ca_c = Ca_f \times \frac{1}{1 - Y}$$

This assumption will introduce only a small error.

7.2 Calculate the $SO_4^{=}$ concentration in the concentrate stream from the $SO_4^{=}$ concentration in the feed solution, from the recovery of the reverse osmosis or nanofiltration system, and from the sulfate ion passage by using the appropriate substitutions in the equation given in 7.1. The simplified equation can be used.

7.3 Calculate the concentration of the major ions in the concentrate stream using the appropriate substitutions in the equation given in 7.1. The simplified equation can be used.

7.4 Calculate the ionic strength of the concentrate stream as follows:

$$I_c = \frac{1}{2} \sum \bar{m}_i Z_i^2$$

where:

I_c = ionic strength of concentrate stream,
$\bar{m}_i$ = molal concentration of ion, i (moles/1000 g of water) in the concentrate stream, and
Z_i = ionic charge of ion, i.

NOTE 3—The molal concentration is calculated as follows:

$$m_i = \frac{C_i}{1000\,MW_i\left[\frac{10^6 - TDS}{10^6}\right]} = \frac{1000\,C_i}{MW_i\left(10^6 - TDS\right)}$$

where:

C_i = concentration of ion, i, in concentrate stream, mg/L,
MW_i = molecular weight of ion, i, and
TDS = total dissolved solids in concentrate stream, mg/L.

7.5 Calculate the ion product (IP_c) for $CaSO_4$ in the concentrate stream as follows:

$$IP_c = \left({}^{m}Ca^{++}\right)_c \left({}^{m}SO_4^{=}\right)_c$$

where:

$\left({}^{m}Ca^{++}\right)_c$ = M Ca^{++} in concentrate, mol/L and
$\left({}^{m}SO_4^{=}\right)_c$ = M $SO_4^{=}$ in concentrate, mol/L.

7.6 Compare IP_c for $CaSO_4$ with the solubility product (K_{sp}) of $CaSO_4$ at the ionic strength of the concentrate stream (Fig. 1).[3] If $IP_c > K_{sp}$, $CaSO_4$ scaling will occur and adjustment is required.

NOTE 4—Some suppliers use a safety factor. Check with the supplier of the reverse osmosis or nanofiltration device to determine if some fraction

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[3] Marshall, W. L. and Slusher, R., "Solubility to 200°C of Sulfate and its Hydrates in Sea Water and Saline Water Concentrates and Temperature, Concentration Limits," *Journal of Chemical and Engineering Data*, Vol 13, No. 1, 1968, p. 83.

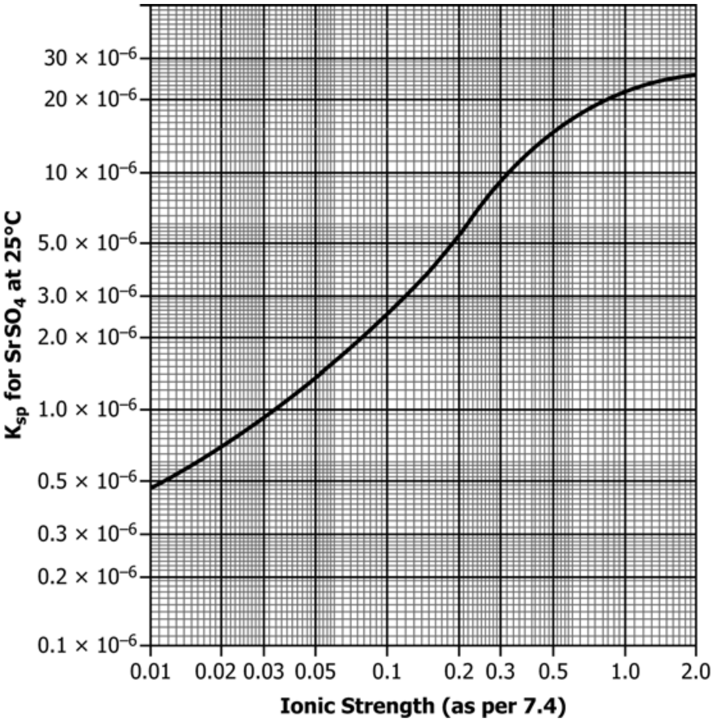

FIG. 2 K_{sp} for $SrSO_4$ versus Ionic Strength

of the K_{sp}, for example 0.8 K_{sp}, should be used to compare with IP_c.

7.7 Determine the scaling potential for $SrSO_4$ using the appropriate substitution in steps 7.1 to 7.4. Compare IP_c for $SrSO_4$ with the K_{sp} of $SrSO_4$ at the ionic strength of the concentrate stream (Fig. 2).[4]

7.8 Determine the scaling potential for $BaSO_4$ using the appropriate substitutions in steps 7.1 – 7.4. Compare IP_c for $BaSO_4$ with the K_{sp} of $BaSO_4$ at the ionic strength of the concentrate stream (Fig. 3).[4]

8. Adjustments for Scale Control

8.1 If the IP_c for $CaSO_4$, $SrSO_4$, and $BaSO_4$ is less than the K_{sp} or the recommended fraction of K_{sp}, a higher recovery can be used with respect to scaling by the various salts. Reiteration of the calculations at higher recovery can be used to determine the maximum conversion with respect to scaling by the various salts.

8.2 If the IP_c for $CaSO_4$, $SrSO_4$, or $BaSO_4$ is greater than the K_{sp} of the recommended fraction of K_{sp}, a lower recovery must be used to prevent scaling. Reiteration of the calculations at lower recovery can be used to determine the allowable recovery with respect to scaling by the various salts.

8.3 If the maximum allowable recovery is lower than desired, sodium cycle ion exchange (softening) can be used to remove all or part of the Ca^{++}, $Sr^{+\,+}$, and Ba^{++}. This will permit higher recovery of the reverse osmosis or nanofiltration system with respect to scaling by the various salts.

8.4 Lime softening with lime or lime plus soda ash will decrease the Ca^{++} concentration and thus permit higher conversion with respect to scaling by $CaSO_4$.

8.5 Addition of a scale inhibitor to the feed stream permits operation of the reverse osmosis or nanofiltration system above the K_{sp} value. Check with supplier of the reverse osmosis or nanofiltration system to determine compatibility of inhibitors, concentration of the inhibitor needed, and amount by which the K_{sp} can be exceeded when a scale inhibitor is used.

9. Reverse Osmosis or Nanofiltration in Operation

9.1 Once a reverse osmosis or nanofiltration system is operating, the scaling potential of $CaSO_4$, $SrSO_4$, and $BaSO_4$ can be directly calculated from the analyses of the concentrate stream and compared with the projected scaling potential calculated above.

10. Use of Computers for the Determination of Scaling Potential

10.1 The preceding calculations are adaptable to simple computer analysis.

11. Keywords

11.1 barium; calcium; membrane fouling; membrane scaling; nanofiltration; reverse osmosis; strontium; sulfate scaling

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[4] Davis, J. W. and Collins, A. G., "Solubility of Barium and Strontium Sulfates in Strong Electrolyte Solutions," *Environmental Science and Technology*, Vol 5, No. 10, 1971, p. 1039.

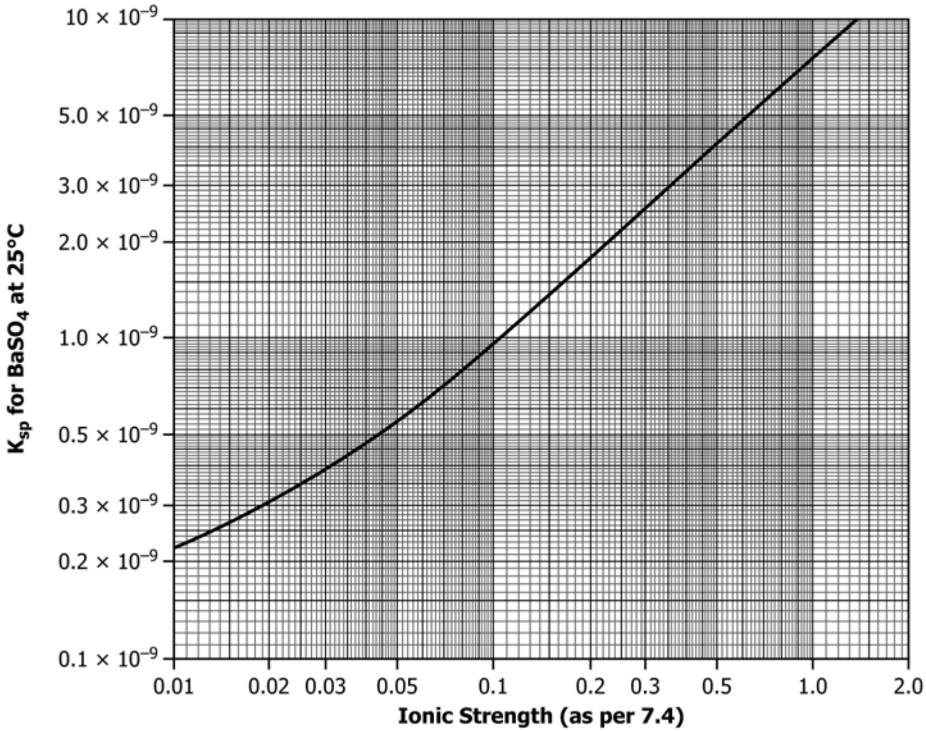

FIG. 3 K_{sp} for $BaSO_4$ versus Ionic Strength

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