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Standard Practice for Calculation of Supersaturation of Barium Sulfate, Strontium Sulfate, and Calcium Sulfate Dihydrate (Gypsum) in Brackish Water, Seawater, and Brines[1]

This standard is issued under the fixed designation D 4328; 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.

ϵ^1 Note—Keywords were added editorially in July 1993.

1. Scope

1.1 This practice covers the calculation of supersaturation of barium sulfate, strontium sulfate, and calcium sulfate dihydrate (gypsum) in brackish water, seawater, and brines in which barium, strontium, and calcium ions either coexist or exist individually in solution in the presence of sulfate ions.

1.2 This practice is not applicable for calculating calcium sulfate dihydrate supersaturation if the temperatures of saline waters under investigation exceed 95°C. At temperatures above 95°C, hemianhydrate and anhydrite would be major insoluble forms.

1.3 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 511 Test Methods for Calcium and Magnesium in Water[2]
D 512 Test Methods for Chloride Ion in Water
D 513 Test Methods for Total and Dissolved Carbon Dioxide in Water[2]
D 516 Test Method for Sulfate Ion in Water[2]
D 1129 Terminology Relating to Water[2]
D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[2]
D 3352 Test Method for Strontium Ion in Brackish Water, Seawater, and Brines[3]
D 3370 Practices for Sampling Water from Closed Conduits[2]
D 3561 Test Method for Lithium, Potassium, and Sodium Ions in Brackish Water, Seawater, and Brines by Atomic Absorption Spectrophotometry[3]
D 3651 Test Method for Barium in Brackish Water, Seawater, and Brines[3]
D 3986 Test Method for Barium in Brines, Seawater, and Brackish Water by Direct-Current Argon Plasma Atomic Emission Spectroscopy[3]

3. Terminology

3.1 *Definitions:* For definitions of terms used in this practice, refer to Terminology D 1129.

4. Significance and Use

4.1 This practice covers the mathematical calculation of the supersaturation of three principal sulfate scaling compounds found in industrial operations. Application of this standard practice to the prediction of scale formation in a given system, however, requires experience. The calculations tell the user if a water, or mixture of waters, is in a scaling mode. Whether or not scale will in fact form, how quickly it will form, where it will form, in what quantities, and what composition are subject to factors beyond the scope of this practice. An objective evaluation of the relative likelihood of scale formation can be made, however, based on how supersaturated a given water, or mixture of waters, is.

5. Procedure

5.1 Collect water samples for compositional analysis in accordance with Practices D 3370 and Specification D 1192.

5.2 Determine the calcium and magnesium concentrations in accordance with Test Methods D 511.

5.3 Determine the barium concentration in accordance with Test Methods D 3651 or D 3986.

5.4 Determine the strontium concentration in accordance with Test Method D 3352.

5.5 Determine sodium and potassium concentrations in accordance with Test Method D 3561.

5.6 Determine sulfate ion concentration in accordance with Test Method D 516.

5.7 Determine chloride ion concentration in accordance with Test Methods D 512.

5.8 Determine carbonate and bicarbonate ion concentrations

[1] This practice is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.02.

in accordance with Test Methods D 513.

5.9 Determine the concentrations of all other major inorganic constituents that may be present in the water under investigation in accordance with appropriate test methods in *Annual Book of ASTM Standards,* Vols 11.01 and 11.02.

5.10 Determine temperature and pressure of the water system under investigation.

6. Calculation of Ionic Strength

6.1 Calculate the ionic strength of the water under investigation as follows:

$$\mu = \frac{1}{2}\Sigma C_i Z_i^2 \tag{1}$$

where:

μ = ionic strength,
C_i = molal concentration of each ion in solution, and
Z_i = charge number of ion, i.

7. Calculation of Barium Sulfate Supersaturation (Refer to Appendix X1)

7.1 Calculate barium sulfate solubility in the water under investigation, using the equation as follows:

$$S = (\sqrt{X^2 + 4K} - X)/2 \tag{2}$$

where:

S = solubility, moles of solute per kilogram of water corrected for the common ion effect,
K = solubility product constant (molal) at the ionic strength, temperature and pressure of the water under investigation. For $BaSO_4$ refer to Appendix X2, and
X = molal excess of soluble common ion.

7.2 Calculate the amount of barium sulfate, moles per kilogram of water, in the sample based on the lesser of the barium or sulfate ion concentration.

7.3 If the amount of $BaSO_4$ in the sample (7.2) is less than its calculated solubility (7.1), the water in question is undersaturated with respect to $BaSO_4$. If the amount of $BaSO_4$ present is greater than its solubility, the water is supersaturated with respect to $BaSO_4$. Calculate the amount of supersaturation as the difference between the two values:

$$\text{supersaturation} = \text{concentration} - \text{solubility} \tag{3}$$

NOTE 1—Supersaturation may also be calculated directly from the equation **(1)**[4]

$$([Ba^{++}] - y)([SO_4=] - y) = K \tag{4}$$

where:

Ba^{++} = concentration of barium, molal,
$SO_4=$ = concentration of sulfate, molal,
y = excess (supersaturation) of $BaSO_4$, molal, and
K = solubility product constant (molal) of $BaSO_4$ at test conditions.

The value X may then be determined from the quadratic equation (see Appendix X1):

$$X = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}$$

[4] The boldfaced numbers in parentheses refer to a list of references at the end of this standard.

Report $BaSO_4$ supersaturation in molal terms of the weight of $BaSO_4$ per volume of water, mg/L.

$$BaSO_4 \text{ supersaturation, mg/L} = BaSO_4, (\text{molal}^2) \times 10^3 \times 233 \times \left(\frac{1000 \times D}{\frac{TDS}{1000}} + 1000 \right)$$

where D = sample density.

8. Calculation of Strontium Sulfate Supersaturation (Refer to Appendix X1)

8.1 Calculate strontium sulfate solubility using the same steps described for $BaSO_4$(Section 7), but substituting the appropriate values for $SrSO_4$ in Eq 2 (Refer to Appendixes Appendix X3 or Appendix X4).

NOTE 2—If barium sulfate supersaturation exists, the amount of sulfate available for strontium sulfate will be less by the amount of sulfate equivalent to the calculated $BaSO_4$ supersaturation.

NOTE 3—If carbonate ions are present, strontium carbonate may precipitate. The amount of strontium may then be corrected by that required for strontium carbonate precipitation prior to the calculation of $SrSO_4$ solubility. **(6)** Practically speaking, however, due to the extremely low solubility of $SrCO_3$, this correction may usually be omitted.

8.2 Calculate the amount of strontium sulfate moles per kilogram water in the sample based on the lesser of the strontium or remaining sulfate ion concentration.

8.3 If the amount of $SrSO_4$ in the sample (8.2) is less than its calculated solubility (8.1), the water in question is undersaturated with respect to $SrSO_4$. If the amount of $SrSO_4$ present is greater than its solubility, the water is supersaturated with respect to $SrSO_4$. Calculate the amount of supersaturation, moles per kilogram water by difference (Eq 3), or by substituting appropriate data in Eq 4 (Note 1).

8.3.1 Report $SrSO_4$ supersaturation in terms of the weight of $SrSO_4$ per volume of water as follows:

$$SrSO_4 \text{ supersaturation mg/L} = SrSO_4, (\text{molal}) \times 10^3 \times 184 \times \left(\frac{1000 \times D}{\frac{TDS}{1000} + 1000} \right)$$

9. Calculation of Calcium Sulfate Supersaturation (Refer to Appendix X1)

9.1 Calculate calcium sulfate solubility using the same steps described for $BaSO_4$(Section 7), but substituting the appropriate values for $CaSO_4$ in Eq 2 (Refer to Appendix X5).

9.2 Calculate the amount of calcium sulfate moles per kilogram in the sample based on the lesser of the calcium or remaining sulfate ion.

9.3 If the amount of $CaSO_4$ in the sample (9.2) is less than its calculated solubility (9.1), the water in question is undersaturated with respect to $CaSO_4$. If the amount of $CaSO_4$ present is greater than its solubility, the water is supersaturated with respect to $CaSO_4$. Calculate the amount of supersaturation moles per kilogram by difference (Eq 3) or by substituting appropriate data in Eq 4 (Note 1).

9.3.1 Report $CaSO_4$ supersaturation in terms of the weight of $CaSO_4 \cdot 2H_2O$ (gypsum) per volume of water after converting moles per data obtained above to mg/L as follows:

$CaSO\cdot 2H_2O$ supersaturation, mg/L
$= CaSO_4\cdot 2H_2O_2$, moles/kg $\times$ 172.17 $\times 10^3 \times D$

10.

11. Keywords

11.1 barium sulfate; brines; calcium sulfate dihydrate; strontium sulfate

APPENDIXES

(Nonmandatory Information)

X1. SAMPLE CALCULATION OF BaSO4 SUPERSATURATION AT 95°CPrecision and Bias

Analysis of Water				Ionic Strength	
Component Ions	mg/L	moles per litre [A]	molal [A] Concentration	Z^2	$\mu = ½\Sigma,Z,^2$ (Section 6)
Na	27 120	1.180	1.214	1	1.214
Ca	10 890	0.272	0.280	4	1.120
Mg	1679	0.69	0.071	4	0.284
Ba	6.4	0.000044	4.52×10^{-5}	4	>0.001
Sr	444	0.00506	521.42×10^{-5}	4	0.021
Cl	64 870	1.830	1.883	1	1.883
SO_4	1210	0.012596	1296.14×10^{-5}	4	0.052
HCO_3	317	0.005	0.005	1	0.005
	TDS = 106 536				Total ionic strength = 2.29
	Density = 1.078 g/ml				K_{BaSOr} at 95° (Appendix X1) = 83.22×10^{-9}

[A]

$$\text{Convert moles/L to molal} = \text{moles/L} \times \frac{1000}{(\text{Sp gr} \times 1000) - \frac{TDS}{1000}}$$

$$= \text{moles/L} \times \frac{1000}{1078 - 106.5}$$

$$= \text{moles/L} \times 1.029$$

X1.1 *$BaSO_4$ solubility (refer to 7.1)*

$$S = (\sqrt{X^2 + 4K} - X)/2$$

where:

X = molal excess of common ion (in this case SO_4),
X = $(1296.14 \times 10^{-5}) - (4.52 \times 10^{-5})$
$= 1291.62 \times 10^{-5}$
$4K$ = $4(83.22 \times 10^{-9}) = 332.88 \times 10^{-9}$, or 3328.8×10^{-10}
S = $[\sqrt{(1291.62 \times 10^{-5})^2 + (3328.8 \times 10^{-10})}$
$- (1291.62 \times 10^{-5})]/2$

Solubility $S = 0.644 \times 10^{-5}$ molal

X1.2 *$BaSO_4$ present (refer to 7.2):*

X1.2.1 Ba present = 4.52×10^{-5} molal

X1.2.2 SO_4 present = 1296.14×10^{-5} molal

X1.2.3 Based on lower value (Ba), $BaSO_4$ present = 4.52×10^{-5} molal

X1.3 *Amount of $BaSO_4$ supersaturation (refer to 7.3)*

X1.3.1 $BaSO_4$ present based on Ba^{++} = 4.52×10^{-5} molal

X1.3.2 Calculated $BaSO_4$ solubility, $S = 0.64 \times 10^{-5}$ molal

X1.3.3 $BaSO_4$ excess; i.e. supersaturation = 3.88×10^{-5} molal; or 8.8 mg/L of sample

X1.4 Useful Information:

	Mol Weight	Equivalent Weight	Gravimetric Conversion Factors
Ba	137.33	68.66	Ba × 1.6995 = $BaSO_4$
Ca	40.08	20.04	Ca × 3.3967 = $CaSO_4$
Sr	87.62	43.81	Sr × 2.0963 = $SrSO_4$
SO_4	96.06	48.03	
$BaSO_4$	233.39	116.70	SO_4 × 2.4296 = $BaSO_4$
$CaSO_4$	136.14	68.07	SO_4 × 1.4172 = $CaSO_4$
$CaSO_4\cdot 2H_2O$	172.14	86.07	SO_4 × 1.9121 = $SrSO_4$
$SrSO_4$	183.68	91.84	

X1.5 The amount of supersaturation (excess $BaSO_4$) may also be calculated directly using the expression (Eq 4):

$$([Ba^{++}] - X)\,([SO_4 =] - X) = K_{BaSO4}$$

X1.5.1 Using the molal values from the water analyis above this becomes:

$$([4.52 \times 10^{-5}] - X)\,([1296.14 \times 10^{-5}] - X) = 832.2 \times 10^{-10}$$
$$\text{Multiplying: } (5858.55 \times 10^{-10}) - (1300.66 \times 10^{-5})$$

$$X + X^2 = 832.2 \times 10^{-10}$$

Combining: $X^2 - (1300.66 \times 10^{-5})\,X + 5026.35 \times 10^{-10} = 0$

X1.5.2 Substituting the above coefficients of X in the quadratic equation:

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

and solving, $X = 3.88 \times 10^{-5}$ molal; or 8.8 mg/L of sample.

X2. SOLUBILITY DATA FOR BaSO4·NaCl·H2O SYSTEMS (2)

Solution Ionic Strength, μ	Solubility Product Constant, *K* (Molal)					
	25°C	35°C	50°C	65°C	80°C	95°C
0.1	1.54×10^{-9}	2.00×10^{-9}	2.70×10^{-9}	3.34×10^{-9}	3.76×10	3.97×10^{-9}
0.2	2.70	3.36	4.76	5.93	7.06	7.74
0.4	4.49	5.63	7.92	10.61	13.69	16.13
0.6	6.08	7.74	11.03	15.38	20.45	24.97
0.8	7.74	9.60	13.69	20.16	26.57	33.49
1.0	9.22	11.24	16.38	24.02	32.76	42.02
1.5	12.54	15.38	22.20	32.40	44.94	62.00
2.0	15.63	19.04	27.23	39.60	56.17	78.96
2.5	18.23	21.90	31.33	44.94	63.50	93.64
3.0	20.74	24.65	34.97	49.73	70.23	107.57
3.5	23.41	27.56	38.81	53.82	76.73	120.41
4.0	25.92	30.63	42.44	58.08	82.94	132.50
4.5	28.56	34.23	45.80	63.00	89.40	144.40

X3. SOLUBILITY PRODUCT DATA FOR SrSO42·NaCl·H2O SYSTEMS (3)

Solution Ionic [A] Strength, μ	Solubility Product Constant, *K* (Molal)	
	40°C (104°F)	71°C (160°F)
0.1	0.250×10^{-5}	0.160×10^{-5}
0.2	0.390	0.250
0.3	0.505	0.345
0.4	0.617	0.440
0.5	0.723	0.518
0.75	1.02	0.785
1.0	1.26	1.04
1.25	1.48	1.25
1.5	1.68	1.41
1.75	1.86	1.57
2.0	2.00	1.68
2.25	2.09	1.76
2.5	2.14	1.81
2.75	2.16	1.84
3.0	2.17	1.86
3.25	2.19	1.87
3.50	2.20	1.88

[A] The above table may be used to interpolate the solubility product (*K*) for $SrSO_4$ in brines at 0 psig. The interpolated values can be substituted in Eq 2 (Section 6) for estimating the solubility (*S*) of $SrSO_4$. For more precise *K* values at temperatures up to 300°F (149°C) and pressures up to 3000 psig add SI unit, refer to Appendix X4.

X4. Equation for Calculating SrSO4 Solubility (4)

X4.1 Experimental $SrSO_4$ solubility data have been reduced to the following regression equation for calculating the solubility product constant (K) at various solution ionic strengths over a temperature range of 100 to 300°F (38 to 149°C) and pressures up to 3000 psig. The equation is adaptable to computer calculation which can then substitute the value for K in Eq 2 (Section 6) for computing the solubility of $SrSO_4$ at desired conditions.

$$\text{Log } K_{SrSO4} = X/R$$

where:

X = $1/T$,
R = $A+BX+C\mu^{1/2}+D\mu+EZ^2+FXZ+G\mu^{1/2}Z$,
Z = pressure (psig),
μ = solution ionic strength,
T = temperature,° K.

X4.1.1 Coefficients of the above equation for R are as follows:

A = 0.266948×10^{-3}
B = -244.828×10^{-3}
C = -0.191065×10^{-3}
D = 53.543×10^{-6}
E = -1.383×10^{-12}
F = 1.103323×10^{-6}
G = -0.509×10^{-9}

X5. SOLUBILITY PRODUCT DATA FOR CaSO42·NaCl·H2O SYSTEMS (5)

Solution Ionic Strength, μ	Solubility Product Constant, K (Molal)			
	10°C	35°C	50°C	80°C
0	1.02×10^{-4}	1.27×10^{-4}	1.25×10^{-4}	0.89×10^{-4}
0.1	3.04	3.29	3.31	2.82
0.2	4.99	5.23	5.28	4.67
0.3	6.87	7.11	7.17	6.44
0.4	8.68	8.91	8.96	8.13
0.5	10.41	10.64	10.68	9.75
0.6	12.07	12.30	12.30	11.30
0.7	13.65	13.88	13.85	12.78
0.8	15.16	15.39	15.32	14.18
0.9	16.60	16.83	16.71	15.52
1.0	17.96	18.20	18.02	16.79
1.25	21.05	21.29	20.96	19.70
1.5	23.69	23.93	23.46	22.22
1.75	25.90	26.12	25.52	24.39
2.0	26.67	27.88	27.18	26.22
2.25	29.03	29.22	28.47	27.73
2.5	30.00	30.15	29.40	28.92
2.75	30.60	30.71	30.01	29.81
3.0	30.84	30.90	30.32	30.42
3.25	30.77	30.77	30.36	30.73
3.5	30.39	30.34	30.15	30.76
3.75	29.76	29.66	29.73	30.51
4.0	28.90	28.75	29.13	29.97
4.25	27.85	27.66	28.37	29.14
4.5	26.65	26.43	27.49	28.02
4.75	25.34	25.13	26.52	26.58
5.0	23.98	23.80	25.48	24.83

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