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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<sup>1</sup>

This standard is issued under the fixed designation D4328; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope-~~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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

### 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

[D511 Test Methods for Calcium and Magnesium In Water](#)

[D512 Test Methods for Chloride Ion In Water](#)

[D513 Test Methods for Total and Dissolved Carbon Dioxide 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](#)

[D3370 Practices for Sampling Water from Closed Conduits](#)

[D3561 Test Method for Lithium, Potassium, and Sodium Ions in Brackish Water, Seawater, and Brines by Atomic Absorption Spectrophotometry](#)

[D3651 Test Method for Barium in Brackish Water, Seawater, and Brines](#)

[D3986 Test Method for Barium in Brines, Seawater, and Brackish Water by Direct-Current Argon Plasma Atomic Emission Spectroscopy](#)

### 3. Terminology

3.1 ~~Definitions—Definitions:~~ For definitions of terms used in this practice, refer to Terminology [D1129](#).

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### 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,

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee [D19](#) on Water and is the direct responsibility of Subcommittee [D19.05](#) on Inorganic Constituents in Water. Current edition approved ~~June 1, 2013~~May 1, 2018. Published ~~July 2013~~May 2018. Originally approved in 1984. Last previous edition approved in ~~2008~~2013 as [D4328 – 08](#)-[D4328 – 08 \(2013\)](#). DOI: ~~10.1520/D4328-08R13~~10.1520/D4328-18.

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

\*A Summary of Changes section appears at the end of this standard

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. However, based on how supersaturated a given water or mixture of waters is, an objective evaluation of the relative likelihood of scale formation can be made.

NOTE 1—There are several personal computer (PC) type programs that are both available commercially and publicly that will perform these calculations.

## 5. Procedure

- 5.1 Collect water samples for compositional analysis in accordance with Practices **D3370**.
- 5.2 Determine the calcium and magnesium concentrations in accordance with Test Methods **D511**.
- 5.3 Determine the barium concentration in accordance with Test Methods **D3651** or **D3986**.
- 5.4 Determine the strontium concentration in accordance with Test Method **D3352**.
- 5.5 Determine sodium and potassium concentrations in accordance with Test Method **D3561**.
- 5.6 Determine sulfate ion concentration in accordance with Test Method **D516**.
- 5.7 Determine chloride ion concentration in accordance with Test Methods **D512**.
- 5.8 Determine carbonate and bicarbonate ion concentrations in accordance with Test Methods **D513**.
- 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:

$$\mu = \frac{1}{2} \sum C_i Z_i^2 \quad (1)$$

where:

- $\mu$  = 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:

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

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  $\text{BaSO}_4$  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  $\text{BaSO}_4$  in the sample (7.2) is less than its calculated solubility (7.1), the water in question is undersaturated with respect to  $\text{BaSO}_4$ . If the amount of  $\text{BaSO}_4$  present is greater than its solubility, the water is supersaturated with respect to  $\text{BaSO}_4$ . Calculate the amount of supersaturation as the difference between the two values:

$$\text{supersaturation} = \text{concentration} - \text{solubility} \quad (3)$$

NOTE 2—Supersaturation may also be calculated directly from the equation (1).<sup>3</sup>

$$([\text{Ba}^{++}] - y)([\text{SO}_4^{--}] - y) = K \quad (4)$$

where:

- $\text{Ba}^{2+}$  = concentration of barium, molal,
- $\text{SO}_4^{2-}$  = concentration of sulfate, molal,

<sup>3</sup> The boldfaced numbers in parentheses refer to a list of references at the end of this standard.

$y$  = excess (supersaturation) of  $\text{BaSO}_4$ , molal, and  
 $K$  = solubility product constant (molal) of  $\text{BaSO}_4$  at test conditions.

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

$$X = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A} \quad (5)$$

Report  $\text{BaSO}_4$  supersaturation in molal terms of the weight of  $\text{BaSO}_4$  per volume of water, mg/L.

$$\begin{aligned} & \text{BaSO}_4 \text{ supersaturation, mg/L} \\ & = \text{BaSO}_4, (\text{molal}^2) \times 10^3 \times 233 \times \left( \frac{1000 \times D}{\text{TDS}} + 1000 \right) \\ & \text{BaSO}_4 \text{ supersaturation, mg/L} \end{aligned} \quad (6)$$

$$= \text{BaSO}_4, (\text{molal}^2) \times 10^3 \times 233 \times \left( \frac{1000 \times D}{\text{TDS}} + 1000 \right)$$

~~where:~~ 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  $\text{BaSO}_4$  (Section 7), but substituting the appropriate values for  $\text{SrSO}_4$  in [Eq 2](#) (refer to [Appendix X3](#) or [Appendix X4](#)).

NOTE 3—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  $\text{BaSO}_4$  supersaturation.

NOTE 4—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  $\text{SrSO}_4$  solubility (2). Practically speaking, however, due to the extremely low solubility of  $\text{SrCO}_3$ , 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  $\text{SrSO}_4$  in the sample (8.2) is less than its calculated solubility (8.1), the water in question is undersaturated with respect to  $\text{SrSO}_4$ . If the amount of  $\text{SrSO}_4$  present is greater than its solubility, the water is supersaturated with respect to  $\text{SrSO}_4$ . Calculate the amount of supersaturation, moles per kilogram water by difference ([Eq 3](#)), or by substituting appropriate data in [Eq 4](#) ([Note 2](#)).

8.3.1 Report  $\text{SrSO}_4$  supersaturation in terms of the weight of  $\text{SrSO}_4$  per volume of water as follows:

$$\begin{aligned} & \text{SrSO}_4 \text{ supersaturation mg/L} \\ & = \text{SrSO}_4, (\text{molal}) \times 10^3 \times 184 \times \left( \frac{1000 \times D}{\text{TDS}} + 1000 \right) \\ & \text{SrSO}_4 \text{ supersaturation mg/L} \end{aligned} \quad (7)$$

$$= \text{SrSO}_4, (\text{molal}) \times 10^3 \times 184 \times \left( \frac{1000 \times D}{\text{TDS}} + 1000 \right)$$

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

9.1 Calculate calcium sulfate solubility using the same steps described for  $\text{BaSO}_4$  (Section 7), but substituting the appropriate values for  $\text{CaSO}_4$  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  $\text{CaSO}_4$  in the sample (9.2) is less than its calculated solubility (9.1), the water in question is undersaturated with respect to  $\text{CaSO}_4$ . If the amount of  $\text{CaSO}_4$  present is greater than its solubility, the water is supersaturated with respect to  $\text{CaSO}_4$ . Calculate the amount of supersaturation moles per kilogram by difference ([Eq 3](#)) or by substituting appropriate data in [Eq 4](#) ([Note 2](#)).

9.3.1 Report CaSO<sub>4</sub> supersaturation in terms of the weight of CaSO<sub>4</sub>·2H<sub>2</sub>O (gypsum) per volume of water after converting moles per data obtained above to mg/L as follows:

$$\begin{aligned} & \text{CaSO}_4 \cdot 2\text{H}_2\text{O supersaturation, mg/L} & (8) \\ & = \text{CaSO}_4 \cdot 2\text{H}_2\text{O, moles/kg} \times 172.17 \times 10^3 \times D \end{aligned}$$

**10. Keywords**

10.1 barium sulfate; brines; calcium sulfate dihydrate; strontium sulfate

**APPENDIXES**

(Nonmandatory Information)

**XI. SAMPLE CALCULATION OF BaSO<sub>4</sub> SUPERSATURATION AT 95°C**

Analysis of Water				Ionic Strength		
Component Ions	mg/L	moles Moles per litre-Litre <sup>-1</sup>	molal Molal <sup>A</sup> Concentration	Z <sup>2</sup>	μ = 1/2 ∑ <sub>i</sub> Z <sub>i</sub> <sup>2</sup> (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 <sup>-5</sup>	4	>0.001	
Sr	444	0.00506	521.42 × 10 <sup>-5</sup>	4	0.021	
Cl	64 870	1.830	1.883	1	1.883	
SO <sub>4</sub>	1210	0.012596	1296.14 × 10 <sup>-5</sup>	4	0.052	
HCO <sub>3</sub>	317	0.005	0.005	1	0.005	
TDS = 106 536 Density = 1.078 g/ml				Total ionic strength = 2.29 K <sub>BaSO<sub>4</sub></sub> at 95° (Appendix X1) = 83.22 × 10 <sup>-9</sup>		

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$$\begin{aligned} & \text{Convert moles/L to molal} = \text{moles/L} \times \frac{1000}{(\text{Sp gr} \times 1000) - \frac{TDS}{1000}} \\ & \text{Convert moles/L to molal} = \text{moles/L} \times \frac{1000}{(\text{Sp gr} \times 1000) - \frac{TDS}{1000}} \\ & = \text{moles/L} \times \frac{1000}{1078 - 106.5} \\ & = \text{moles/L} \times 1.029 \\ & = \text{moles/L} \times \frac{1000}{1078 - 106.5} \\ & = \text{moles/L} \times 1.029 \end{aligned}$$

**XI.1 BaSO<sub>4</sub> Solubility (Refer to 7.1):**

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

where:

$$\begin{aligned} X &= \text{molal excess of common ion (in this case SO}_4\text{)}, \\ X &= (1296.14 \times 10^{-5}) - (4.52 \times 10^{-5}) \\ &= 1291.62 \times 10^{-5} \\ 4K &= 4(83.22 \times 10^{-9}) = 332.88 \times 10^{-9}, \text{ or } 3328.8 \times 10^{-10} \\ S &= [\sqrt{(1291.62 \times 10^{-5})^2 + (3328.8 \times 10^{-10})} \\ &\quad - (1291.62 \times 10^{-5})] / 2 \end{aligned}$$

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

X1.2 *BaSO<sub>4</sub> Present (Refer to 7.2):*

X1.2.1 Ba present =  $4.52 \times 10^{-5}$  molal

X1.2.2 SO<sub>4</sub> present =  $1296.14 \times 10^{-5}$  molal

X1.2.3 Based on lower value (Ba), BaSO<sub>4</sub> present =  $4.52 \times 10^{-5}$  molal

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X1.3 *Amount of BaSO<sub>4</sub> Supersaturation (Refer to 7.3):*

X1.3.1 BaSO<sub>4</sub> present based on Ba<sup>2+</sup> =  $4.52 \times 10^{-5}$  molal

X1.3.2 Calculated BaSO<sub>4</sub> solubility,  $S = 0.64 \times 10^{-5}$  molal

X1.3.3 BaSO<sub>4</sub> excess; that is, supersaturation =  $3.88 \times 10^{-5}$  molal; or 8.8 mg/L of sample

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