



Water Chemistry and Pretreatment

Calcium Carbonate Scale Prevention

Brackish Water

For brackish waters with TDS < 10,000 mg/L in the concentrate stream, the Langelier Saturation Index (LSI) is used to express the scaling potential for calcium carbonate /6/.

The following data are needed to calculate the LSI of the concentrate stream (LSI_c):

Ca_f = Calcium concentration in feed as CaCO₃, mg/L

TDS_f = Concentration of total dissolved solids in the feed, mg/L

Alk_f = Alkalinity in feed as CaCO₃, mg/L

pH_f = pH of the feed solution

T = Temperature of the feed solution

Y = Recovery of the reverse osmosis system, expressed as a decimal

Calculations

1. Calculate the calcium concentration in the concentrate stream, Ca_c, as CaCO₃ in mg/L:

$$Ca_c = Ca_f \left(\frac{1}{1-Y} \right) \quad \text{Eq. 1}$$

2. Calculate the total dissolved solids in the concentrate stream, TDS_c in mg/L:

$$TDS_c = TDS_f \left(\frac{1}{1-Y} \right) \quad \text{Eq. 2}$$

3. Calculate the alkalinity in the concentrate stream, Alk_c, as CaCO₃ in mg/L:

$$Alk_c = Alk_f \left(\frac{1}{1-Y} \right) \quad \text{Eq. 3}$$

4. Calculate the free carbon dioxide content (C) in the concentrate stream by assuming that the CO₂ concentration in the concentrate is equal to the CO₂ concentration in the feed: C_c = C_f. The concentration of free carbon dioxide in the feed solution is obtained from Figure 1 as a function of the alkalinity and the pH of the feed solution.
5. Calculate the pH of the concentrate stream (pH_c) using the ratio of alkalinity Alk_c to free CO₂ in the concentrate, Conversion of calcium and alkalinity to pCa and pAlk.

Brackish Water (Cont.)

6. From Conversion of calcium and alkalinity to pCa and pAlk obtain: pCa as a function of Ca_c , pAlk as a function of Alk_c , "C" as a function of TDS_c and temperature (temperature of the concentrate is assumed equal to temperature of the feed solution).

7. Calculate pH at which the concentrate stream is saturated with $CaCO_3$ (pH_s) as follows:

$$pH_s = pCa + pAlk + "C" \quad \text{Eq. 4}$$

8. Calculate the Langelier Saturation Index of the concentrate (LSI_c) as follows:

$$LSI_c = pH_c - pH_s \quad \text{Eq. 5}$$

Adjustments of LSI_c

In most natural waters, LSI_c would be positive without pretreatment. To control $CaCO_3$ scaling, LSI_c has to be adjusted to a negative value, except if adding a scale inhibitor ([Scale Control-Acid Addition](#) (Form No. 45-D01547-en)) or preventive cleaning ([Scale Control-Preventive Cleaning](#) (Form No. 45-D01550-en)) is applied.

The conditions for $CaCO_3$ scale control are:

$LSI_c < 0$ when no antiscalant is added

$LSI_c \leq 1$ when 20 mg/L sodium hexametaphosphate is in the concentrate stream

$LSI_c > 1$ possible with polymeric organic scale inhibitors. For the maximum LSI_c and required dosages, please refer to the scale inhibitor manufacturer's literature.

If LSI_c is not within the above conditions, adjustments can be made by one of the following means. A new LSI_c can then be calculated:

- The recovery, Y , can be lowered and LSI_c can be calculated as above by substituting a new value for the recovery.
- Decreasing the calcium concentration in the feed solution by means of sodium cycle ion exchange. This will increase the pCa and will therefore decrease the LSI_c . Softening will not change the alkalinity or pH of the feed solution and the slight change in TDS_f may be considered negligible. After softening, the LSI_c can be calculated as above using the lower value for calcium concentration.
- Adding acid (HCl , CO_2 , H_2SO_4 , etc.) to the feed solution changes the Alk_f , C_f , and pH. The slight change in TDS_f can usually be neglected. Acid addition will decrease the LSI_c ; however, since many variables change with acidification, trial and error computations are required to determine the amount of acid needed to obtain the desired LSI_c . The number of trial and error computations required to determine the amount of acid needed can be reduced greatly by using the pH_s calculated in Eq. 4. Since pH_c will usually be 0.5 units higher than the pH_f , the first computation can be made with an acidified feed solution that is 0.5 units lower than the pH_s .

Brackish Water (Cont.)

For an assumed pH (pH_{acid}), obtained from addition of acid to the feed solution, obtain the ratio of $\text{Alk}_{\text{acid}}/\text{C}_{\text{acid}}$ from Conversion of calcium and alkalinity to pCa and pAlk. From this ratio, Alk_f and C_f , calculate the mg/L of acid used (x). For example, for H_2SO_4 addition (100%):

$$\frac{\text{Alk}_{\text{acid}}}{\text{C}_{\text{acid}}} = \frac{\text{Alk}_f - 1.02x}{\text{C}_f + 0.90x} \quad \text{Eq. 6}$$

Calculate the total alkalinity of the acidified feedwater (Alk_{acid}) and the CO_2 content in the acidified feedwater (C_{acid}) as follows:

$$\text{Alk}_{\text{acid}} = \text{Alk}_f - 1.02x \quad \text{Eq. 7}$$

$$\text{C}_{\text{acid}} = \text{C}_f + 0.90x \quad \text{Eq. 8}$$

Using Alk_{acid} and C_{acid} for the new pH, calculate the LSI_c .

If HCl (100%) is used for acidification, Eq. 6 is:

$$\frac{\text{Alk}_{\text{acid}}}{\text{C}_{\text{acid}}} = \frac{\text{Alk}_f - 1.37y}{\text{C}_f + 1.21y} \quad \text{Eq. 9}$$

where:

y = HCl (100%), mg/L

Reverse Osmosis and Nanofiltration in Operation

Once a reverse osmosis or nanofiltration system is operating, the Langelier Saturation Index can be directly calculated from the analysis of Alk_c , Ca_c , TDS_c , and pH_c of the concentrate stream and compared with the projected LSI_c .

Use of Computers

The LSI_c and the acid dosage required to adjust a certain LSI_c can be determined using a personal computer and the WAVE (Water Application Value Engine) computer program. The WAVE computer program can be downloaded here, <http://www.dupont.com/water/design-software.html>.

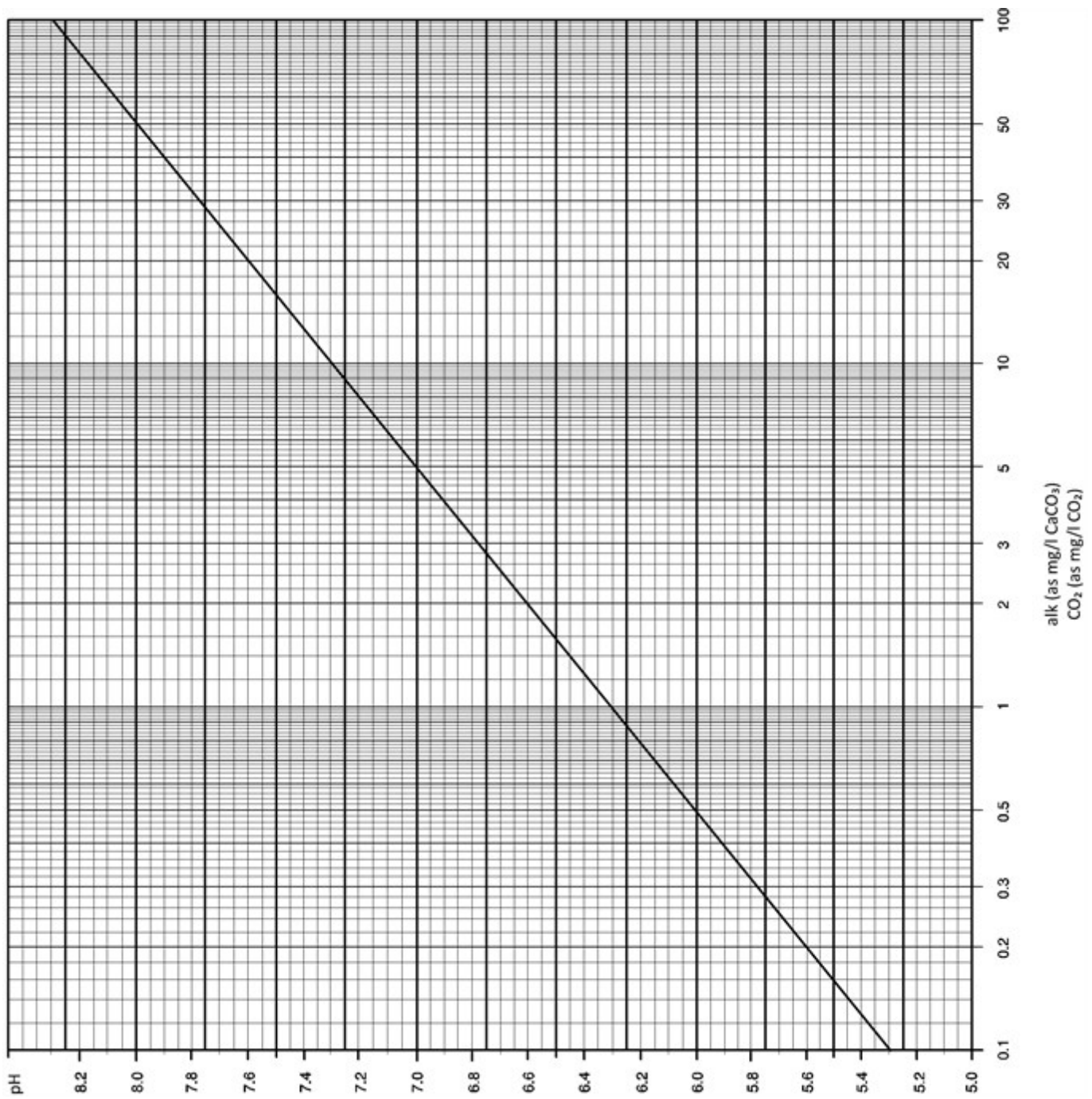


Figure 1: pH versus methyl orange alkalinity/free CO₂

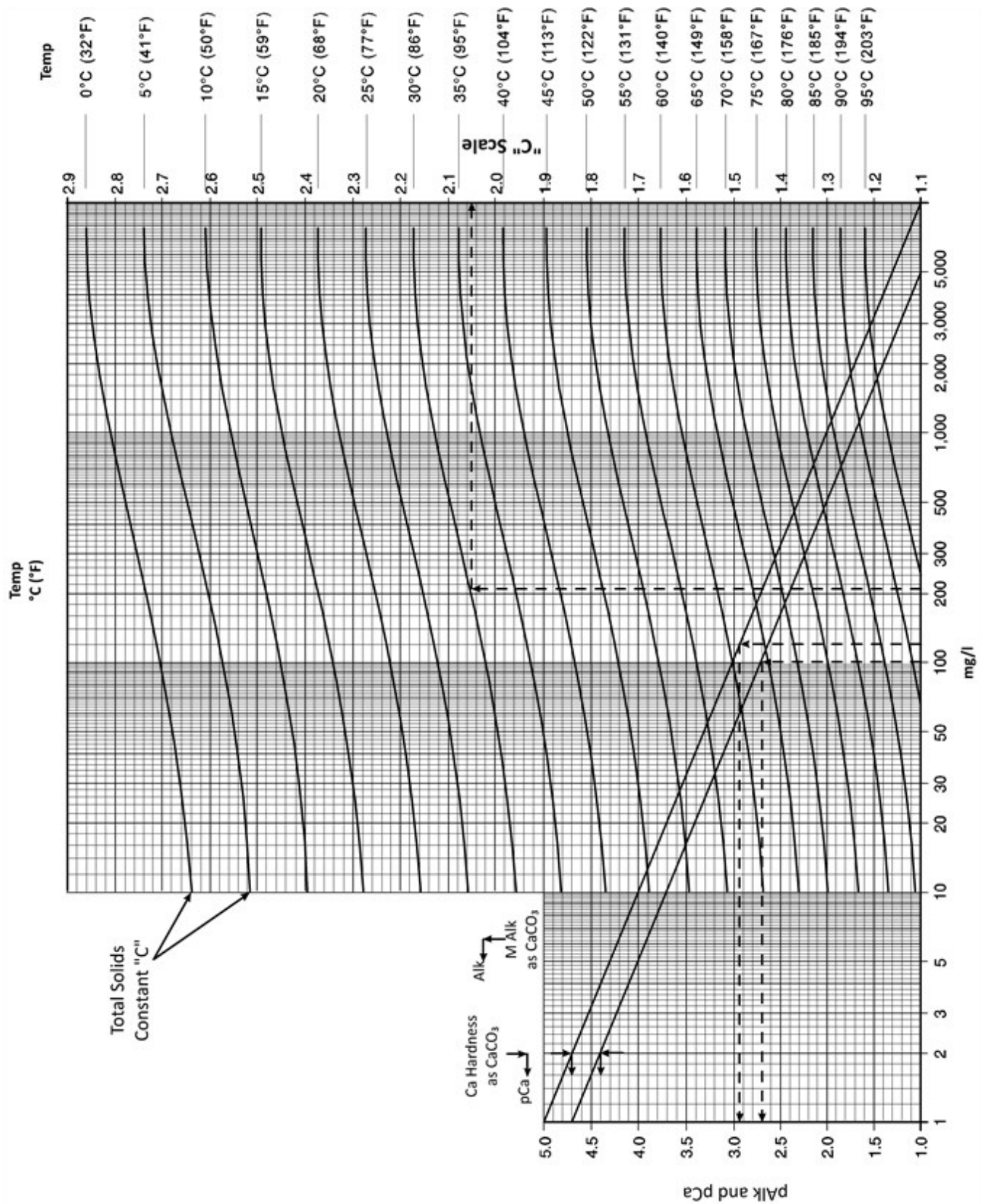


Figure 2: Langlier saturation index

Seawater

For high-salinity brackish waters with TDS > 10,000 mg/L in the concentrate stream and for seawaters, the Stiff & Davis Stability Index (S&DSI) is used to express the scaling potential for calcium carbonate. The data needed to calculate the S&DSI of the concentrate stream are the same as the data needed to calculate the LSI ([Calcium Carbonate Scale Prevention](#) (Form No. 45-D01552-en)). Additionally, the molal concentrations of all ions in the feed solution are required, at least of all major ions (i.e., Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , and Cl^-).

Calculations /7/

1. Calculate the calcium concentration in the concentrate stream, Ca_c , as CaCO_3 in mg/L:

$$\text{Ca}_c = \text{Ca}_f \left(\frac{1}{1-Y} \right) \quad \text{Eq. 10}$$

2. Calculate the alkalinity in the concentrate stream, Alk_c , as CaCO_3 in mg/L:

$$\text{Alk}_c = \text{Alk}_f \left(\frac{1}{1-Y} \right) \quad \text{Eq. 11}$$

3. Calculate the ionic strength of the feed stream (I_f):

$$I_f = \frac{1}{2} \sum m_i z_i^2 \quad \text{Eq. 12}$$

4. Calculate the ionic strength of the concentrate stream (I_c):

$$I_c = I_f \left(\frac{1}{1-Y} \right) \quad \text{Eq. 13}$$

5. From Figure 1 in [Calcium Fluoride Scale Prevention](#) (Form No. 45-D01556-en), obtain pCa as a function of Ca_c and pAlk as a function of Alk_c . From Figure 2 in [Calcium Fluoride Scale Prevention](#) (Form No. 45-D01556-en), obtain "K" as a function of concentrate ionic strength and feed temperature.

6. Calculate the pH at which the concentrate stream is saturated with CaCO_3 (pH_s) as follows:

$$\text{pH}_s = \text{pCa} + \text{pAlk} + "K" \quad \text{Eq. 14}$$

7. Calculate the free carbon dioxide content (C) in the concentrate stream by assuming that the CO_2 concentration in the concentrate is equal to the CO_2 concentration in the feed: $C_c = C_f$. The concentration of free carbon dioxide in the feed solution is obtained from Figure 1 as a function of the alkalinity and the pH of the feed solution.

Seawater (Cont.)

8. Calculate the pH of the concentrate stream (pH_c) using the ratio of alkalinity (from Eq. 11) to free CO_2 in the concentrate (from Step 7), (see Figure 1 in [Calcium Carbonate Scale Prevention](#) (Form No. 45-D01552-en)).
9. Calculate the Stiff and Davis Stability Index of the concentrate (S\&DSI_c) as follows:

$$\text{S\&DSI}_c = \text{pH}_c - \text{pH}_s \quad \text{Eq. 15}$$

Adjustments of S\&DSI_c

The S\&DSI_c in the concentrate stream will be positive with most natural high-salinity waters. In order to prevent CaCO_3 precipitation and scaling, the S\&DSI_c has to be adjusted to a negative value by acid dosing. The S\&DSI_c can remain positive, however, if CaCO_3 precipitation is prevented by the dosage of a scale inhibitor (see the "Scale Inhibitor Addition" section in [Scale Control-Acid Addition](#) (Form No. 45-D01547-en)). For the maximum allowed S\&DSI_c and the required dosage, please refer to the scale inhibitor manufacturer's literature.

If the S\&DSI_c is unacceptable based on the above recommendation, adjustments can be made by one of the following means. A new S\&DSI_c can then be calculated.

- The recovery can be lowered and the S\&DSI_c can be calculated as above by substituting a new value for the recovery.
- Decreasing the calcium and alkalinity concentrations in the feed solution by means of lime or lime-soda ash softening will increase the pCa and pAlk and will therefore decrease the pH_s .
- Addition of acid (HCl , CO_2 , H_2SO_4 , etc.) to the feed solution either with or without lime or lime-soda ash softening changes the Alk_f , C_f , and pH . The slight change in f_r can usually be ignored. Acid addition will decrease the S\&DSI_c ; however, since many variables change with acidification, trial and error computations are required to determine the amount of acid needed to obtain the desired S\&DSI_c .

These computations have been described already in the previous section ([Calcium Carbonate Scale Prevention](#) (Form No. 45-D01552-en)). For seawater systems, a dosage of typically 10 mg/L sulfuric acid is required to achieve a pH_f of about 7 and a negative S\&DSI in the concentrate.

RO/NF in Operation

Once an RO or NF system is operating, the S\&DSI_c can be directly calculated from the analysis of Alk_c , Ca_c , pH_c , and l_c of the concentrate stream and compared with the projected S\&DSI_c .

Seawater
(Cont.)

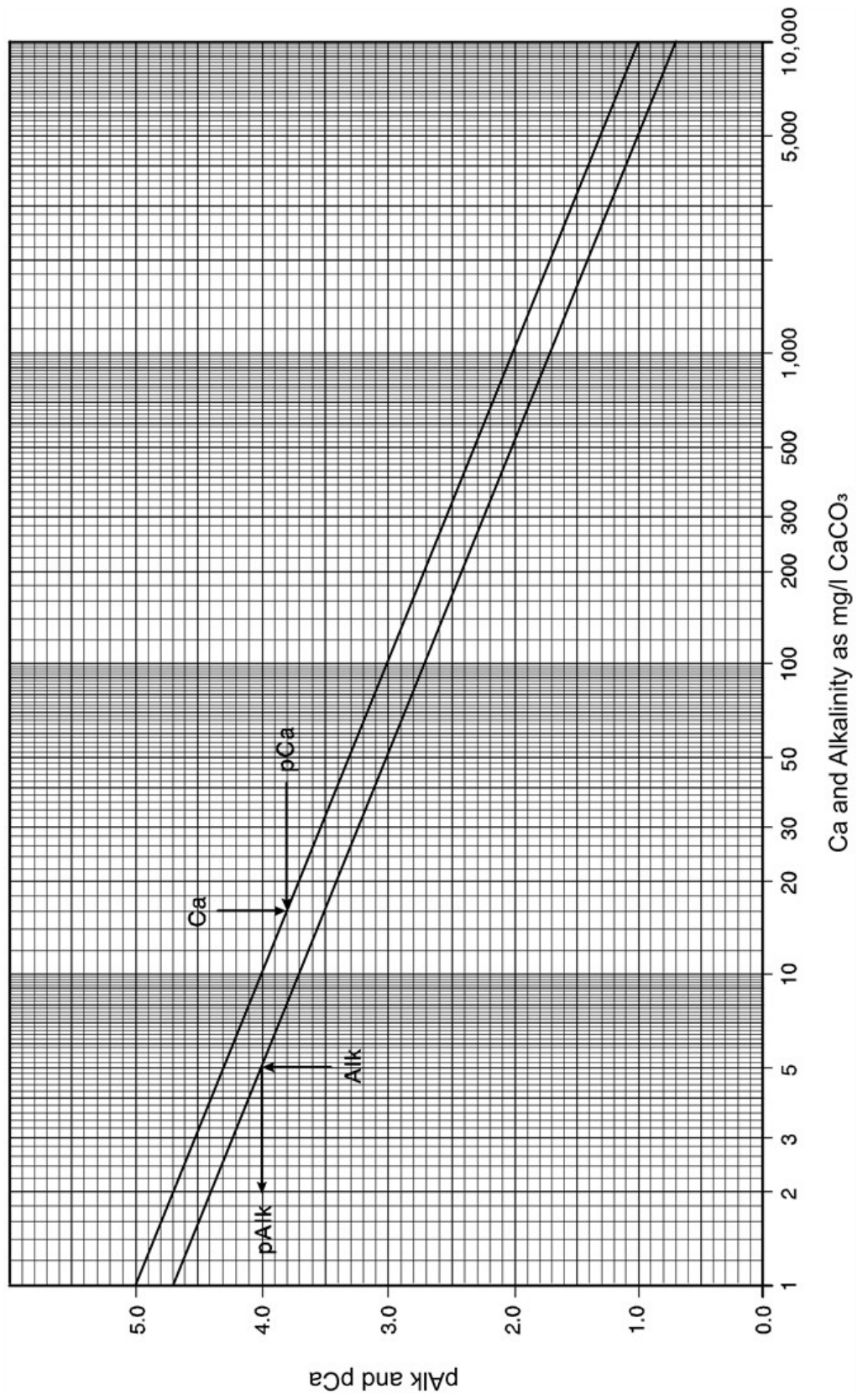


Figure 1: Conversion of calcium and alkalinity to pCa and pAlk

**Seawater
(Cont.)**

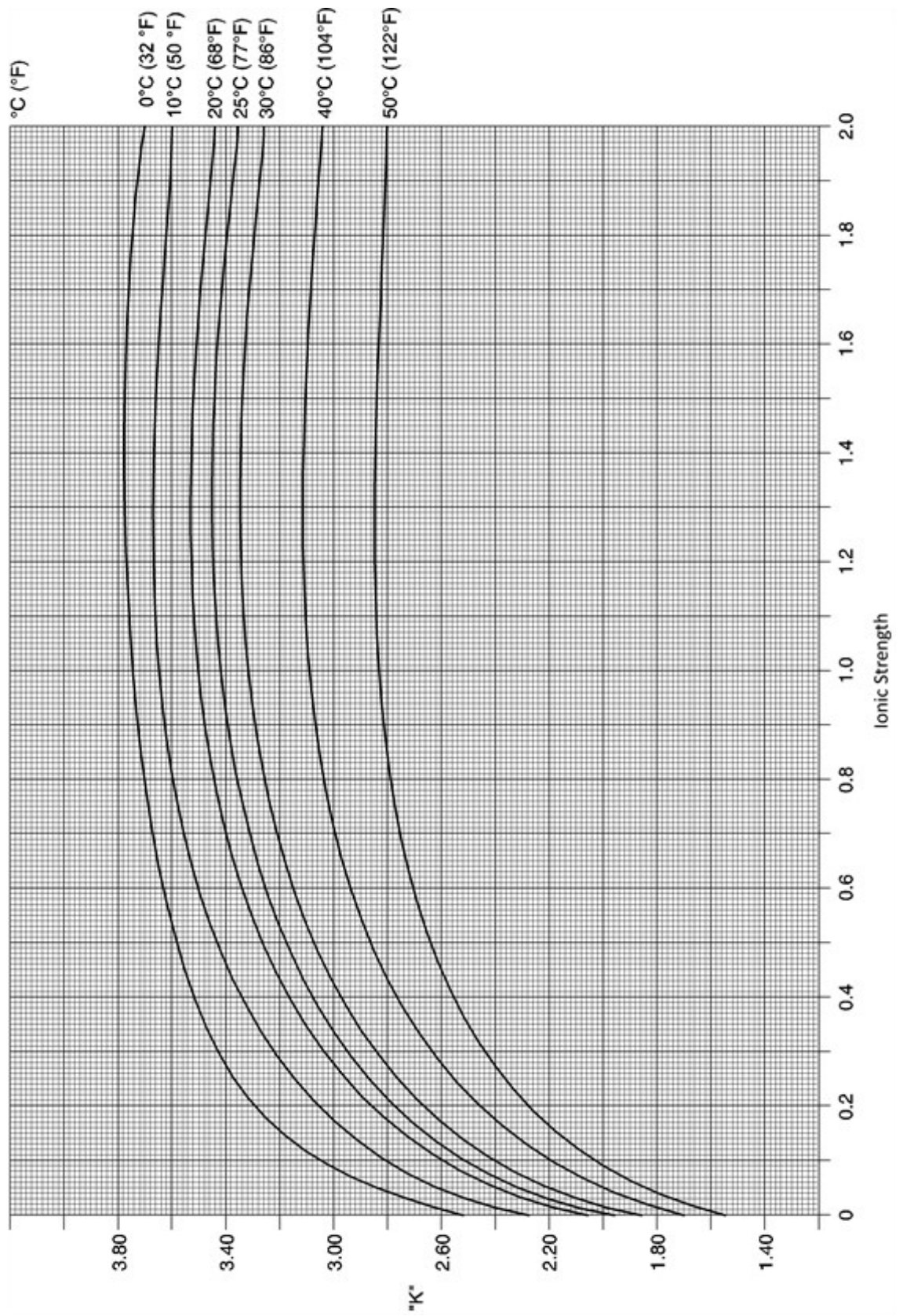


Figure 1: "K" versus ionic strength and temperature

Excerpt from [FilmTec™ Reverse Osmosis Membranes Technical Manual](#) (Form No. 45-D01504-en), Chapter 2, "Water Chemistry and Pretreatment."

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