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Calcium Carbonate Determinations

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CALCIUM CARBONATE DETERMINATIONS

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Summary

for

Dr. Joe Nix

Special Studies 491

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CALCIUM CARBONATE DETERMINATIONS

Calcium compounds are abundant in nature. The carbonate ion may exist in many varieties, such as aragonite and limestone. Of major importance in the following discussion, however, is calcite. Calcium carbonate may well be of animal origin, prime examples being sea shells, coral, and chalk. Dolomite, on the other hand, is a double carbonate of calcium and magnesium. Calcium in natural waters exists mainly as a bicarbonate, $Ca(HCO_3)_2$, which is temporary hardness, or as a sulfate, which is permanent hardness.[1]

From determinations made periodically (every two weeks) since August 1966, a decrease has been found in the calcium content as the water progresses downstream. There are two possible explanations for this: (1)Dilution by tributaries, or (2)Saturation and precipitation of calcium carbonate from the water. Observe the following example:

$$q\,CO_3 = \frac{m_{HCO_3^-} \cdot \gamma_{HCO_3} \cdot K_{HCO_3^-}}{q\,H} = \frac{(1.38 \times 10^{-3})(0.015)(5 \times 10^{-11})}{3.2 \times 10^{-8}}$$

$$= 3.23 \times 10^{-7}$$

$$q\,Ca = \frac{K_{CaCO_3}}{q\,CO_3} = \frac{4.5 \times 10^{-9}}{3.23 \times 10^{-7}} = 1.39 \times 10^{-2} = (13.9 \times 40)\,ppm$$

$$= 556.0\,ppm$$

(actual $q\,Ca^{++}$ never above $25\,ppm$)

As can be seen, this calculation proves that the water is definitely unsaturated, showing a decrease due to dilution.

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[1]Ayres, Gilbert H., 1958, Quantitative Chemical Analysis: Harper and Row, New York, p. 260.

When first developing a method for the calculation of calcium carbonate concentration under conditions of assumed equilibrium, acceptable values were required for the equilibrium constants for calcium carbonate and the bicarbonate ion. The entire basis for determining the extent to which ground water may exist in equilibrium with calcium carbonate lies in a comparison of the calcium concentration found by the chemical analysis with the value obtained by calculating the supposed concentration if the ground water were saturated with calcium carbonate.

The calculation of the activity of the carbonate ion is as follows:
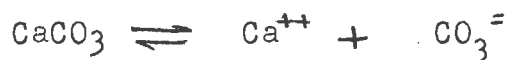
$$CaCO_3 \rightleftharpoons Ca^{++} + CO_3^{=}$$

$$\frac{q_{Ca^{++}} \cdot q_{CO_3^{=}}}{\alpha_{CaCO_3}} = K_{CaCO_3}$$

(q represents activities, and α_{CaCO_3} is unity.)

By definition:

$$\alpha_{Ca^{++}} = m_{Ca^{++}} \cdot \gamma_{Ca^{++}}$$

(m = molality and γ = activity coefficient)

The value for $\gamma_{Ca^{++}}$ and for bicarbonate is given by Geological Survey Water-Supply Paper 1535-D as a function of ionic strength. The ionic strength can be computed as:

$$\mu = \frac{1}{2} \sum m_i z_i^2 ,$$

where m is the molality of the ion (i), which has a charge z in the solution. Most ground waters have a $m_{CO_3^{=}}$ too small to be calculated, although $\alpha_{CO_3^{=}}$ may be calculated from the HCO_3^{-} concentration and the pH.

Using the following equilibrium:

$$HCO_3^- \rightleftharpoons CO_3^= + H^+$$
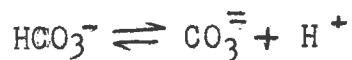
and the Law of Mass Action,

$$\frac{a_{CO_3^=} \cdot a_{H^+}}{a_{HCO_3^-}} = K_{HCO_3^-}$$

Rearrangement and substitution gives

$$a_{CO_3^=} = \frac{m_{HCO_3^-} \cdot \gamma_{HCO_3^-} \cdot K_{HCO_3^-}}{a_{H^+}}$$

The value for m_{HCO_3} is obtained directly from the analysis, while γ_{HCO_3} is given by Geological Survey Water-Supply Paper 1535-D. a_{H^+} is obtained from the pH. Therefore,

$$a_{Ca^{++}} = \frac{K_{CaCO_3}}{a_{CO_3^=}}$$

The above method is applied to ground water analyses by using the following ratio:

$$\frac{\text{Analyzed } Ca^{++}(ppm) - \text{Calculated } Ca^{++}(ppm)}{\text{Analyzed } Ca^{++}(ppm)}$$

Of course, this method is susceptible to error, just as other determinations. The greatest source for error in carbonate determinations is in the pH measurements. Either due to temperature changes or changes in CO_2 content, the true pH of the natural waters is often falsely determined when making laboratory tests. This is the primary reason for testing the pH of samples taken in the field, and not in the laboratory.

Other factors contributing to carbonate errors are the temperature and concentration of the ions in the water. The error caused by laboratory determinations and calculation of ionic strength actually does not affect the value of the activity coefficients, and, as a result, creates no significant change in the calculated values. When testing for calcium alone, trouble is often caused by the presence of strontium, for it shows up and is determined as calcium.

When reporting the value of bicarbonate, which represents alkalinity, error is caused by the contribution of other substances, such as carbonate, borate, phosphates, and silicates, all of which contribute to water alkalinity.

As was mentioned, changes in temperature, ionic strength, or pH may certainly change the carbonate content in natural waters. What has actually happened is that the condition of equilibrium between the water and the carbonate has been shifted. These changes may be caused by bacterial action, by water movement to different temperatures and pressures, or by mixing of waters (such as tributaries) from other sources having different temperatures and ionic strengths.[2]

[2]Back, William, 1961, Calcium Carbonate Saturation in Ground
Water, From Routine Analyses: Geological Survey
Water-Supply Paper 1535-D, pp. 1-13.

12-188

Ca
Ppm

STATION

(STATIONS 1-10 FOLLOW CADDO RIVER DOWNSTREAM)

10 Millimeters to the Centimeter