Calcium is one of the major components of bones and an adequate dietary calcium intake is necessary to achieve peak bone mass and minimize bone loss with aging. The adequate intake of calcium is 1300 mg/day, but it varies depending on gender and age.

Besides its role in bone health, calcium has been associated with other health benefits including lowering the risk of colorectal cancer and lowering blood pressure, with some potential negative effects also associated with an excess in the consumption of this mineral.

Besides the calcium naturally present in foods, its salts are often added to process foods to increase their calcium content or as additives with various functions. The solubility of calcium salts is highly dependent on pH and changes on this parameter during processing or storage on foods can favor or prevent salt precipitation. For example, tricalcium phosphate, presents the following solubility equilibrium

\[
\ce{Ca3(PO4)2 (s) \rightleftharpoons 3Ca^{2+} (aq) + 2PO4^{3-} (aq)}
\]

The solubility product constant for this equilibrium or \( K_{sp} \) is \( 2.0 \times 10^{-29} \) mol\(^5\) dm\(^{-15}\), which results in a solubility equal to \( 7.13 \times 10^{-7} \) mol dm\(^{-3}\).
If acid is added to this solution, some of the phosphate ions become protonated and transformed into \( \text{HPO}_4^- \) ions.

\[
\text{PO}_4^{3-} + \text{H}_3\text{O}^+ \rightleftharpoons \text{HPO}_4^- + \text{H}_2\text{O}
\]

As a result, the concentration of the phosphate ion is reduced. According to the Le Chatelier's principle, the system will respond to this reduction by trying to produce more phosphate ions. Some solid \( \text{Ca}_3(\text{PO}_4)_2 \) will dissolve, and the equilibrium will be shifted to the right. If enough acid is added, the phosphate-ion concentration in the solution can be reduced so as to make the ion product \( Q = c_{\text{Ca}^{2+}} \times c_{\text{PO}_4^{3-}} \) smaller than the solubility product \( K_{\text{sp}} \) so that the precipitate dissolves.

A similar effect can be achieved by using a sequestering anion for calcium, such as citrate. Binding of calcium-ions to citrate will decrease the concentration of "free" calcium-ions. The equilibrium will then shift to the left with further dissolution of \( \text{Ca}_3(\text{PO}_4)_2 \). Both pH control and sequestering agents are strategies used to maintain calcium ions in solution in the formulation of foods fortified with calcium.

**More Salts of Weak Acids and Exceptions**

Other precipitates involving basic anions show similar behavior in acidic pH. These are precipitates in which the anion is basic; i.e., they are the salts of weak acids. Virtually all the carbonates, sulfides, hydroxides, and phosphates which are sparingly soluble in water can be dissolved in acid. Thus, for instance, we can dissolve precipitates like \( \text{ZnS} \), \( \text{Mg(OH)}_2 \), and \( \text{Ca}_2(\text{PO}_4)_3 \) because all the following equilibria

\[
\text{ZnS(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})
\]

\[
\text{Mg(OH)}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})
\]

\[
\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})
\]

can be shifted to the right by attacking the basic species \( \text{S}^{2-} \), \( \text{OH}^- \), and \( \text{CO}_3^{2-} \) with hydronium ions.

Even though low pH can favor the solubility of salts of weak acids, very occasionally we find an exception to this rule. Mercury(II) sulfide, \( \text{HgS} \), is notorious for being insoluble. The solubility product for the equilibrium

\[
\text{HgS(s)} \rightleftharpoons \text{Hg}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})
\]

is so minute \( (4 \times 10^{-53}) \) that not even concentrated acid will reduce the sulfide ion sufficiently to make \( Q \) smaller than \( K_{\text{sp}} \).

**Undesirable effects**

There are cases where the shift in a solubility-product equilibrium caused by a decrease in pH may be undesirable. One example of this is the so called acid rainfall, which can occur when oxides of sulfur and other acidic air pollutants are removed from the atmosphere by its own humidity and rain. In some parts of the United States pH values as low as 4.0 have been observed. These acid solutions dissolve marble and limestone (\( \text{CaCO}_3 \)) causing considerable property damage. This is especially true in Europe, where some statues and other works of art have been almost completely destroyed over the last half century. This phenomenon is also responsible for the formation of caves, the erosion of coral reefs, and damage of teeth by acids in foods.
Figure \( \PageIndex{3} \) Shifting of pH of ocean water accelerates erosion of coral reefs.

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References

2. http://dietary-supplements.info.nih...calcium.asp#h2

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