FROM CALCITE TO PORTLAND CEMENT

Calcite [calcium carbonate, $CaCO_3$] is a mineral that needs little introduction. It is the most abundant carbonate mineral and second only to quartz [silicon dioxide, SiO_2] in overall crustal abundance. It crystallizes in the trigonal system (a hexagonal subsystem), has a Mohs hardness of 3.0, and specific gravity of 2.7-3.0. Calcite crystals occur in an exceptionally broad variety of habits, many of which strikingly beautiful.

Very little of the huge amount of calcite in the Earth's crust occurs as collectible crystals, however. Most exists in granular, compact, massive, and earthy forms, most notably as microcrystals that are the primary mineral component of limestone. By definition, limestone is a marine sedimentary rock that contains at least 50 percent calcite. As the raw material for the manufacture of lime and cement, limestone is used by industry in enormous quantities.

Lime (also known as quicklime, burnt lime, or caustic lime) is calcium oxide (CaO) and is produced by calcining finely ground limestone. In the calcining process, ground, high-grade limestone is heated nearly to its fusion temperature to drive off carbon dioxide from the calcite according to the simple reaction $CaCO_3=CO_2 + CaO$. Lime is an alkaline, white powder that is employed in the manufacture of glass, paper, masonry mortar, whitewash, and many other products. It is also used as a water-softening and soil-conditioning agent, in leather-tanning and sugar-refining processes, and even as a medicinal antacid.

The bulk of all quarried limestone, however, is processed into the key raw material for the manufacture of portland cement, the world's most widely used, inexpensive, and durable construction material.

Portland cement is primarily a mixture of tricalcium silicate [$(CaO)_3 \cdot SiO_2$], tricalcium aluminate [$(CaO)_3 \cdot Al_2O_3$], and dicalcium silicate [$(CaO)_2 \cdot SiO_2$]. It is made from limestone and any inexpensive source of silica and aluminum oxides such as clay, shale, or blast-furnace slag. Along with limestone, these raw materials are ground together and fed into long, rotary kilns. First, heat calcines the calcite into calcium oxide. Then, at temperatures of about 2,800° F., the entire mixture fuses and reacts chemically. The end product is "clinker," a gray-brown, chunky mixture of calcium aluminates and silicates that, when ground into a fine powder, becomes ready-to-mix cement.

When combined with water, cement's components break down into caustic calcium hydroxide and a gel-like mix of hydrated calcium silicates and aluminates. But with a slight loss of water, these compounds recrystallize into non-hydrated silicates and aluminates, "setting up" as an interlocking mass of tiny crystals. In use, cement is mixed with an aggregate material—sand or gravel—and sets up to form a solid, hard, very durable concrete.

Although this basic cement-manufacturing process is simple enough, it actually took thousands of years to develop. The ancient Egyptians used the first lime-based cements, mixtures of calcined limestone and quartz sand, to construct many of their pyramids. The Greeks built their temples with similar types of cement.

But lime-quartz cements do not produce truly durable concretes. Quartz, which is largely inert, has a dense, compact crystalline structure into which calcium hydroxide molecules cannot penetrate and react, thus restricting bonding only to the surface of the sand particles. This limits the overall strength of the concrete and, no less importantly, prevents it from setting up and hardening underwater.

The Romans developed the first modern, lime-based cement by replacing the traditional sand with a volcanic ash obtained from Mount Vesuvius. Unlike quartz sand, the volcanic ash, rich in various silicates and aluminum oxides and already naturally calcined by volcanic heat, has a porous structure. The addition of water to the Roman cement, the powdery, porous volcanic-ash particles provided a huge surface area to maximize the reaction with the calcium hydroxide. The result was a concrete as strong as modern concretes—as demonstrated by the many examples of Roman architecture, such as the Coliseum and Pantheon, that are still standing today.

The formula for Roman cement was lost for 1,400 years before being recreated in England in the early 1800s. The English cement, which employed clay rather than volcanic ash, became known as portland cement, because its concrete matched the color, hardness, and durability of the gray, Jurassic Period limestone that makes up the country rock of England's Portland Peninsula.

An estimated 1.6 *billion* tons of portland cement are manufactured worldwide each year. That production requires the annual mining of nearly a billion tons of calcite in the form of limestone. This makes calcite by far the most widely mined mineral in the world—as well as one of the most collectible.

Steve Voynick

Steve has worked with the Mineral of the Month Club since 2002. As a former hardrock miner, he has mined Colorado molybdenum, Alaska gold, Arizona copper, and Wyoming uranium. Eight of his ten books deal with topics of minerals, mineral collecting, mining, and gemstones. He has written more than 1,000 articles and is a contributing editor and science columnist with *Rock & Gem* magazine. His work has also appeared in *The Mineralogical Record* and *Lapidary Journal*. He is a former member of the board of directors of the National Mining Hall of Fame & Museum