

HISTORICAL NOTE

Hydraulic Cement: Lost and Found

In 1756, John Smeaton, a British engineer, was presented with the challenge of building a sturdy lighthouse on a site where two earlier lighthouses had fallen. The location was Eddystone, off the coast of Cornwall, where navigating conditions were treacherous and shipwrecks frequent. The previous lighthouses, each made of wood, had collapsed in stormy weather, and Smeaton was determined to use stone this time. His problem was finding a cement that would endure under water—a hydraulic cement. Since the method of making such a material was not well understood, Smeaton undertook a systematic study of hydraulic cements.

The first hydraulic cements are attributed to the Greeks, whose addition of a volcanic tuff from the Island of Santorini (so-called Santorin earth) to burned limestone produced cement that could harden under water. The ancient Romans added a tuff called “pozzolana” from the region of Pozzuoli near Naples at the base of Mt. Vesuvius. This “pozzolana cement” was used to hold up structures that are still standing such as the Coliseum in Rome and the Pont du Gard aqueduct at Nîmes in France. In general, the use of a strong mortar made the construction of thinner walls possible. Cement can thus be credited with inspiring some of the graceful architecture of Roman civilization.

But no one knew why pozzolana cement worked as it did. Clearly, some material in the volcanic-earth additive turned a nonhydraulic cement into a hydraulic one, but chemistry had not progressed far enough to provide an analysis. A Roman writer named Vitruvius described the Roman methods of making cement, but his speculations on the mechanisms at work were burdened by the alchemical theories popular at the time. Nonetheless, his surviving writings are credited by some for the later revival of hydraulic cements.

When the Roman Empire fell, the “secret” of hydraulic cement disappeared with it. Cements continued to be used, but the omission of volcanic earth, and the general lack of care in burning the lime to a sufficiently high temperature, rendered these mortars nonhydraulic. The quality of the cement generally depended on the chemistry of the limestone in the local quarry. If by chance the limestone contained some of the silica and alumina compounds found in the volcanic tuff, the cement might be of high quality, and at least semihydraulic. But those with little of these cementitious materials would not hold up under water. This state of affairs

continued until the 18th century.

So Smeaton knew of the ancient hydraulic cements at the time of his Eddystone assignment, but was generally surrounded by inferior nonhydraulic varieties. The only contemporary example he could follow was that of Holland, a notoriously water-logged country that had succeeded in building sea defenses by combining “tarras” (a local type of pozzolana) with lime to form a hydraulic cement widely known as “tarras mortar.” Before beginning his experiments, Smeaton toured Holland in 1754–1755. He saw that the Dutch formulation worked, but wanted to know why it worked.

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Smeaton studied the effects of four variables on cement quality: the type of lime, the type and quantity of tuff added, the use of fresh or salt water in the mix, and the addition of varying proportions of gypsum. After formulating an experimental mix, he formed the mortar into a ball two inches in diameter, then let it sit in air to set before being submerged in water.

“What happened to the ball in this state,” he wrote, “was the criterion by which I judged of the validity of the composition for our purposes.”

The results were surprising. When he began his experiments, it was generally considered that the harder, purer limestones were preferable over the softer, clayey ones for use as mortars. But Smeaton found just the opposite: the clayey limestones formed much stronger cements than the hard limestones.

“An admixture of clay in the composition of a limestone might be the most certain index of the validity of a limestone for aquatic buildings,” Smeaton concluded.

Later, chemists would show that it is precisely the hydrated aluminosilicate clays that provide the necessary reactants to turn the calcium carbonate into the strong calcium aluminate and calcium silicate cementitious materials. Smeaton built his Eddystone lighthouse in 1760

using equal parts of siliceous limestone from the Blue Lias formation at Aberthaw in South Wales, and pozzolana from Civita Vecchia in Italy. But the quest to understand and ultimately to manufacture synthetic cements had just begun.

Spurred by the industrial revolution and laws like the London Building Act of 1774 that mandated the use of fire-resistant stuccos and concretes in place of exposed timbers in new construction, the search for cementitious raw materials flourished. In 1796, James Parker of Northfleet found that the nodules of limestone called “septaria” found mainly along the coast of the Isle of Sheppey made an excellent cement when burned at high temperatures and ground into powders. This material, which Parker patented under the name “Roman Cement,” enjoyed great popularity until mining of the septaria within 50 feet of the clay cliffs was banned in 1845 due to the environmental damage it was causing. Other sources, such as Medina cement from the Isle of Wight and Calderwood cement from Calder Glen in Scotland, were also exploited until natural deposits were depleted.

But chemistry was now sufficiently advanced to provide insight. In 1813, a scientist named Descotels wrote, “It appears very probable that the essential condition for a limestone to furnish good lean lime is that it contain a large quantity of siliceous material disseminated in very fine particles.”

Five years later, L.J. Vicat in France and J.F. John in Holland independently summarized the accumulated data and expressed what was becoming obvious: In the absence of natural deposits of limestone having the necessary proportions of clay compounds, an artificial mixture of clay and limestone would suffice.

“We see that, by being able to regulate the proportions, we can give to the face-tious lime whatever degree of energy we please, and cause it at pleasure to equal or surpass the natural limes,” Vicat wrote. This fundamental understanding of the composition and reactions of calcium-, silica-, and alumina-containing raw materials freed manufacturers from seeking better limestone quarries and tuff deposits; they could instead concentrate on optimizing formulations and manufacturing processes.

Joseph Aspdin, a British bricklayer from Leeds, in 1824 patented the first “Portland Cement,” so named because when it hardened it resembled the stone obtained from the quarries in Portland, England. But Aspdin’s product appears to

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be no more than a minor variant on the standard Roman cements of the time, and certainly not deserving of the reputation that later Portland cements have gained.

Rather, it was probably I.C. Johnson to whom credit for the discovery of the key to modern Portland cement should be given. In 1845, Johnson's experiments with higher calcining temperatures produced a vitrified material that was initially discarded as unusable; later, cement

samples made of these vitrified materials proved to be superior in color and hardness. Variations on these original mixtures and further experimentation led to the practice of "incipient vitrification" that is the basis for the high quality of modern Portland cements.

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FOR FURTHER READING: Richard K. Meade, *Portland Cement: Its Composition,*

Raw Materials, Manufacture, Testing, and Analysis, Third Edition (The Chemical Publishing Co., Easton, PA, 1926); Norman Davey, *A History of Building Materials* (Phoenix House, London, 1961); Robert H. Bogue, *The Chemistry of Portland Cement* (Reinhold Publishing Corp., New York, 1955); and Edison Portland Cement Company, *The Romance of Cement* (Livermore and Knight Co., New York, 1926).