“Portland Cement: Its Constitution, Properties, and Manufacture – Regions Where the Different Materials Are Found”

Written for *Mines and Minerals*, by Richard K. Meade,
Author of *The Chemical and Physical Examination of Portland Cement*

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(An unrelated article that is included in the images of the above article is entitled, “Intermediate Side track for Tail-Rope Haulage,” written for *Mines and Minerals*, by L. L. Logan, pp. 485.)

PORTLAND CEMENT.

Its Constitution, Properties, and Manufacture—Regions Where the Different Materials Are Found.

Written for "Mines and Minerals," by Richard K. Meade, Author of "The Chemical and Physical Examination of Portland Cement."

In the English Channel, nine miles off the coast of Cornwall and to the west of Plymouth harbor, there rises from 150 fathoms of water a group of gneiss rocks. These Eddystone crags are covered daily by the tide and until the erection upon them of the first lighthouse, a wooden affair, in 1696, many ships had been wrecked upon them. This flimsy structure was entirely too frail to stand the fierce onslaughts of wind and wave, and three years after its completion it and its architect were blown into the channel. The next lighthouse, also of wood, had a longer life but was destroyed by fire. When the time came to build a third tower of warning, the necessity of erecting a more enduring structure was understood, and one, John Smeaton, an English engineer, was appointed to set about the difficult task. It is not our purpose to tell of his difficulties and of his achievements, of how he took the trunk of an oak tree for a model and constructed on these rocks one of the most wonderful pieces of engineering of his time, but rather of a discovery which he made in connection with his work.

Lime mortar will not harden out of contact with the air. Lime, CaO, when slacked forms a hydroxide, $Ca(OH)_2$, this on exposure to the air absorbs or unites with the carbon dioxide, always present in the atmosphere, and forms calcium carbonate; this latter change or reaction causes the hardening of mortar. General Treusart who had occasion, in 1822, to demolish one of the bastions of Strasburg, erected by Vauban in 1666, found that in the interior the lime after the lapse of 156 years was as soft as though it was the first day it was laid.

From the nature of the structure designed by Smeaton, which was to stand enormous strains of wave and wind, a good foundation was necessary. Smeaton knew how unsatisfactory lime mortar was and how impossible it was to get it to harden under water out of contact with the air. He therefore undertook a series of experiments looking to the discovery of a material which would harden under water. As the result of his researches, he exploded the theory previously held that the hardest and purest limestones made the best lime, and found in in its place that the clayey limestones would when properly burned produce a lime or cement which would harden out of contact with the air and under water.

From 1757, the date of Smeaton's discovery, to 1824 nothing was added to man's knowledge of cement, but in the latter year, one Joseph Aspdin, a bricklayer of Leeds, England, obtained a patent for the manufacture of a cement, which he made from burning an artificial mixture of the scrapings from roads repaired with limestone (consequently powdered limestone) and clay. This material he called Portland cement, from the similarity of its appearance, when hardened, to that of the sandstone from the Portland quarries in England. It must be observed that Smeaton prepared his hydraulic cement from the rock just as it came from the quarry, the name hydraulic coming from its property of hardening under water. He used a blue lias stone found in Alberthaw, England, which contained a considerable proportion of clay. Aspdin, on the other hand, made an artificial mixture of limestone and clay. This distinction still holds for Portland cement, and differentiates it from all other hydraulic cements—it must be prepared from an artificial mixture containing the proper elements in the proportions found to give best results in practice. Why the Portland should be superior to the natural or pure rock cements is not hard to understand when one reflects that, given limestone and clay it will be easy to mix these two in any desired proportion while it would be very difficult to find in nature the two already mixed in just this proportion. The nearest approach to such a natural cement rock is to be found in our own Lehigh Valley, around Easton and Allentown, Pa., and in Belgium.

Aspdin immediately began the manufacture of his new found Portland cement and other firms, lessees under his patents, began to make it also. The new cement found extensive use quite soon, and it was used largely in the Thames Tunnel, constructed in 1828, in spite of its cost, about $4.50 per cask.

It was not until 1852 that the first cement works were established in Germany, near Stettin. Other works followed. These at first used English methods, but as the German chemists studied the problem more closely, they began to originate ways and tricks of their own. They inaugurated a system of testing their product and aimed carefully to get the best results as shown by their tests. The outcome of this was soon to displace English by German cement outside of England, and England is only just now wakening to the fact that what should be her industry has slipped from her, and English manufacturers are now trying vainly to regain lost export trade.

In America, the first Portland cement works were started at Coplay, Lehigh County, Pa., by the late D. O. Saylor. This plant, now the Coplay Cement Co., is still in operation, and its cement, "Saylor's Brand," ranks with the best cements of the world. Natural rock cement had been made in America at Rosendale, Ulster County, N. Y., since 1828, at Louisville, Ky., since 1829, and at various other points in New York, Kentucky, Ohio, Michigan, and Maryland, and the hydraulic properties of the cements made from the limestones of the Lehigh Valley were known, but Saylor's plant at Coplay was the first to manufacture genuine Portland cement. Other plants to follow the one at Coplay, in America, were the Empire Portland Cement Co., of Warners, N. Y.; the Buckeye, near Bellefontaine, Ohio, and the Western, at Yankton, S. D.

It is interesting to note that the section within a radius of 15 miles of Coplay, the first home of the cement industry in America, now produces over 72 per cent. of the total American output. From this section, in the busy months of the year, over 1,000,000 barrels of cement are shipped on an average. Recently, in one day, November 1, 1901, 21,000 barrels were shipped from the Central mill of the Atlas Portland Cement Co., of Northampton, Pa. It required over a mile and a half of cars to move this quantity. The manufacture of Portland cement has become in the last ten years a recognized established American industry. Its growth in that time has been marvelous. Exactly how rapid the table given below will show.

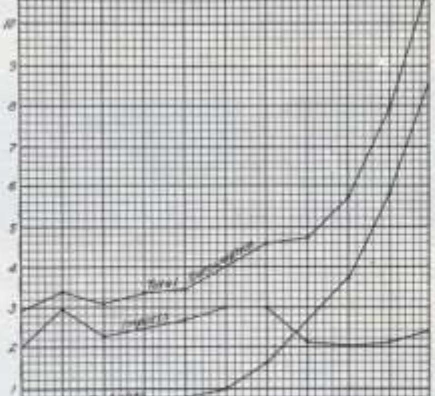


Fig. 1. Graphic Table Report. N. J. State Geologist.

This table also shows us the increasing demand for Portland cement, and the falling off of imports. The domestic production now seems to have caught up with the consumption, as there is a falling off in the imports for the nine months ending September 1, 1901, of 65 per cent. over that of a corresponding period in 1900. Indeed, it is feared that home production will be in excess of the demand when the works now in construction or proposed are in operation. It is hoped, however, that new uses for cement and the establishment of an export trade will relieve this tendency to overstock the market. There is already a picking up in this latter field, and the exports of the last nine months were four times as great as during a corresponding period of 1900.

For a long time the German cements were considered the best. This was due in part to their marked superiority over many of the English brands, but principally to the rigid testing to which the German manufacturer subjected his product and the guarantee, based upon this, which he gave. German cements also tested by German methods will give apparently higher results than American cements tested by American methods, but, tested by the same method, the American cements will give fully as good results. Indeed, in a report to the Mayor of Philadelphia, Mr. Richard H. Humphrey states that the American cements are superior to the German ones. Other engineers also make the statement that many American cements are as carefully made, show as good tests, and prove as satisfactory in practice as the best German cements.

The first Portland cement made by Aspdin, while a great improvement over the natural rock cement of Smeaton, was still a very crude building material in comparison with any of the well-known brands of today. At first the kiln used for burning the cement was the ordinary dome-shaped lime kiln of that time, requiring drawing the fire and recharging. Rules of thumb sufficed for making the mixture of clay and limestone, or else trial tests in small kilns; and the grinding machinery was of the crudest. Today, continuous kilns with large outputs, running night and day until stopped for repairs, have replaced the dome-shaped lime kiln. All plants of any pretentions employ a chemist, who daily analyzes the raw materials and proportions them so as to give the best results, while modern grinding machinery pulverizes the cement clinker so fine that over 90 per cent. of the ground product will pass through a sieve with 100 meshes to the linear inch.

Portland cement must not be confounded with natural, Roman, or Rosendale cement. Portland cement is made by heating to incipient fusion an artificial mixture of limestone and clay or other materials rich in alumina, silica, and lime. Natural cement, on the other hand, is made by heating natural clayey limestones until part of the carbon dioxide is driven off. These limestones are found in various parts of the United States, noticeably, Rosendale, N. Y., Louisville, Ky., Cumberland and Roundtop, Md., Utica, Ill., and Balcony Falls, Va. In the case of either Portland or natural cement the resulting burned mass or clinker, as it is called, is finally ground.

When this powder is mixed with water to a stiff paste and allowed to stand a sufficient time, the paste undergoes chemical change and a solid mass results. This "setting," as it is called, usually requires but a few hours at most. After setting, a slower chemical action sets in, and the mass gradually gains in strength. Usually this gain of strength or hardening extends over a period of from six months to a year—sometimes even beyond this period. Quite a number of chemists have examined into the chemical composition of cement and the changes which it undergoes when it sets. Their results and conclusions are not very concordant, and there is still much room here for investigation. Le Chatelier's ideas are probably nearest the truth. He undertook a very complete series of experiments, in which he not only examined hardened cement and cement clinker, but also made cement of pure lime, silica, and alumina in varying proportions. As the result of his work he concluded that Portland cement was a mixture of tricalcium silicate, $3CaO{\cdot}SiO_2$, and tricalcium aluminate, $3CaO{\cdot}Al_2O_3$. When mixed with water the following change or reaction takes place:

$$2(3CaO{\cdot}SiO_2) + 9H_2O = (CaSiO_3)_2{\cdot}5H_2O + 4Ca(OH)_2$$

$$\left.\begin{matrix}\text{tricalcium}\\ \text{silicate}\end{matrix}\right\}\text{ and }\left\{\text{water}\right\}\text{ give }\left\{\begin{matrix}\text{calcium}\\ \text{silicate}\end{matrix}\right\}\text{ and }\left\{\begin{matrix}\text{calcium}\\ \text{hydroxide.}\end{matrix}\right.$$

The calcium hydroxide formed then unites with the calcium aluminate and the rest of the water as follows:

$$3CaO{\cdot}Al_2O_3 + Ca(OH)_2 + 11H_2O = 4CaOH{\cdot}Al_2O_3{\cdot}12H_2O$$

$$\left.\begin{matrix}\text{tricalcium}\\ \text{aluminate}\end{matrix}\right\}\text{ and }\left\{\begin{matrix}\text{calcium}\\ \text{hydroxide}\end{matrix}\right\}\text{ and }\left\{\text{water}\right\}\text{ give }\left\{\begin{matrix}\text{hydrated basic}\\ \text{calcium aluminate.}\end{matrix}\right.$$

The strength of the cement is due to the tricalcium silicate, the rapidity with which it sets to the tricalcium aluminate. Cement made from lime and silica only, takes a long time to set, but ultimately hardens to a very strong mass. The addition of the alumina, however, shortens the time required for setting. Cements which set moderately slow are likely to give best results, as in the end they will produce the harder mass. In submarine work, quick setting cements are used for obvious reasons.

It is possible from these two formulas $3CaO{\cdot}SiO_2$ and $3CaO{\cdot}Al_2O_3$, to calculate the correct proportion of lime which should be present for various quantities of silica and alumina. In the first formula, for every molecule of silica there are three molecules of lime, and since the molecular weight of silica is 60.4 and of lime 168.3, for every 60.4 pounds of silica present in the compound there should be 168.3 pounds of lime, or 2.78 of lime for 1 of silica.

Silica : lime :: 60.4 : 168.3 :: 1 : 2.78.

Similarly, for every molecule of alumina there should be 3 of lime, or for 102.2 pounds of alumina 168.3 of lime, or 1.65 of lime for 1 of alumina.

Alumina : lime :: 102.2 : 168.3 :: 1 : 1.65.

Hence, combining the two,

% lime = % alumina × 1.65 + % silica × 2.78.

This ratio of the lime to the silica and alumina is called the hydraulic index of the cement. It varies according to various authorities. Newberry gives it as

% lime = % silica × 2.8 + % alumina × 1.1.

The importance of correctly proportioned cement will be well understood when it is known that free lime, that is an excess of lime over that chemically combined with the silica and alumina, causes cement to distort and crack after setting. Beside the silica, lime, and alumina, essential to hydraulic cement, iron, magnesia, and sulphur are always present. Iron oxide forms hydraulic compounds with lime and counts as alumina. The color of cement is also due to the iron. Sulphur confers upon cement slow setting properties, and should be present in less than 2 per cent. of sulphur trioxide in which form it usually exists in cement. Magnesia should not be present in larger proportion than 2 per cent. A larger amount than this causes the cement in time to expand and crack. Below are the analyses of some well-known cements:

	Alpha.	Saylors.	Empire.	Sandusky.	Dyckerhoff.
Silica	22.62	22.68	22.04	23.08	20.64
Alumina	8.76	6.71	6.45	6.16	7.15
Iron oxide	2.66	2.35	3.41	2.90	3.69
Lime	61.46	62.90	60.92	62.38	63.06
Magnesia	2.92	3.14	3.53	1.21	2.33
Sulphur trioxide	1.53	1.88	2.73	1.66	1.39

Of the above brands, the Alpha and Saylors are made in the Lehigh Valley, the Empire at Warners, N. Y.; the Sandusky at Sandusky, Ohio, and the Dyckerhoff near Mainz on the river Rhine in Germany.

It will be seen from the above table, within what narrow limits the percentages of the different constituents usually lie in good cement.

Silica	22.04—23.08
Alumina and iron oxide	9.06—11.42
Lime	60.92—63.06

Theoretically, Portland cement can be made from a great variety of raw materials. Practically for commercial reasons, the range is not so wide, and nearly all cement is made from mixtures of "cement rock" (argillaceous limestone low in magnesia) and limestone, or mixtures of clay and marl, limestone or chalk.

The composition of some of these materials is shown below:

	Alpha Cement Rock, Lehigh Valley.	Sandusky, Ohio.		Yankton, S. D.	
		Marl.	Clay.	Chalk.	Clay.
Silica	14.44	.22	65.41	6.95	58.30
Iron oxide and alumina	5.91	1.62	22.00	6.15	21.10
Lime	42.10	51.42	2.22	45.33	3.90
Magnesia	.37	.25	1.88	.46	2.56
Carbon dioxide	33.48	40.63		35.70	6.05

The "cement rock" of the Lehigh Valley possesses many advantages over other forms of raw material. In it, as will be seen by the above analysis, the silica and alumina are mixed with almost the required amount of lime. Since the mixing has been done by nature it is very intimate and thorough, and the union of the silica and alumina with the lime in burning is assured. Most of this rock is deficient in lime, and the addition of a little pure limestone is necessary to bring the mixture to the correct composition. These materials, however, are rather hard, but since most of the coarser particles are of nearly correct composition, fine grinding is unnecessary. The composition of marl is very similar to that of limestone, and this material is extensively used in the central States. It is soft and unconsolidated, and can be easily and cheaply reduced to the required degree of fineness. Chalk is extensively used in England, Germany, and France for Portland cement making. It lies between marl and limestone in point of hardness, and is similar to these substances in chemical composition. In Michigan, alkali waste, a form of calcium carbonate precipitated in the manufacture of caustic soda, has been used mixed with clay for cement making.

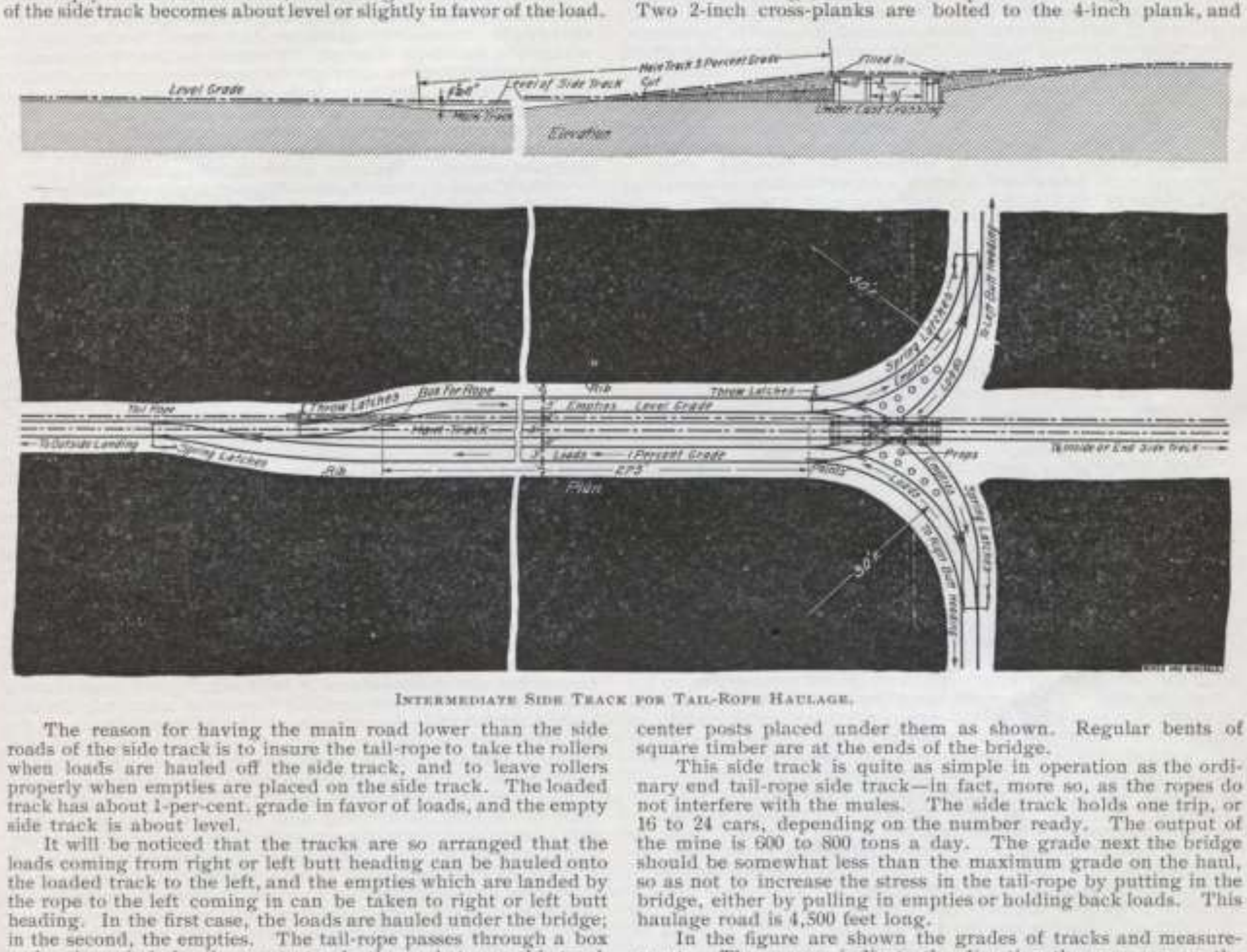
Clay is used extensively as the basis of the silica and alumina in cement mixture. It should be as free as possible from quartz sand, or free silica, as it requires very fine pulverizing of these quartz particles to get them to combine with the lime. If sand is present the amount should be determined, and not calculated as silica in making up the cement mixture, or the resulting cement will probably be over-limed, that is, contain free lime, due to the fact that the sand has not combined with its proportion of the lime, and both are left free. Limestone is not very satisfactory for use with clay, as it is very hard and must be ground very fine to mix properly with the clay. Clay requires several times its own weight of limestone to make a correct cement mixture, and the cost of grinding such large amounts of hard stone is considerable. For the same reason slate and shale, which are solidified clay, are not suitable for cement making. Most of the rocks used for preparing natural cements are unsuitable for the preparation of Portland cement by admixture of limestone, marl, etc., as they contain a high percentage of magnesia. If these are burned at the high temperature (over

2,000° Fahrenheit) necessary to produce Portland cement, they fuse from the excess of magnesia to a glassy slag which shows no hydraulic properties. If burned at a lower temperature, however, one just sufficient to drive off the carbon dioxide, they give a soft yellow clinker, which, when ground, yields a fairly good cement. From the low temperature of burning and consequent saving of fuel, as well as the soft clinker and consequent easy grinding, it follows that the natural cements can be placed upon the market cheaper than Portland cement. When strength and wearing qualities are desired, the Portland cement will prove the cheaper in the long run.

Intermediate Side Track for Tail-Rope Haulage.

Written for "Mines and Minerals," by L. L. Logan.

The accompanying figure shows a plan and elevation of an intermediate side track for a tail-rope haulage in operation at the Slope Mine at Robertsdale, Pa. There are three tracks at this point, the main one in the middle, the loaded one to the left going out, and the empty one to the right. The main track is always kept clear of standing cars. As shown in the figure, it has a grade of about 5 per cent. in favor of the loads, starting from a point near the outside end of the bridge and continuing on this pitch until it is about 6 or 8 inches lower than the loaded and empty tracks on each side, when the grade for the remainder of the side track becomes about level or slightly in favor of the load.



INTERMEDIATE SIDE TRACK FOR TAIL-ROPE HAULAGE.

The reason for having the main road lower than the side roads of the side track is to insure the tail-rope to take the rollers when loads are hauled off the side track, and to leave rollers properly when empties are placed on the side track. The loaded track has about 1-per-cent. grade in favor of loads, and the empty side track is about level.

It will be noticed that the tracks are so arranged that the loads coming from right or left butt heading can be hauled onto the loaded track to the left, and the empties which are landed by the rope to the left coming in can be taken to right or left butt heading. In the first case, the loads are hauled under the bridge; in the second, the empties. The tail-rope passes through a box under the switch for the empty track, thence between this track and the main track. The haulage or main rope keeps the center of the main track throughout. The large sheave wheel is placed at the far end of the inside or end side track. But two pair of latches (those marked throw-latches) need attention.

The mules turn to the left of the loads and pass between these and the rib until they come to the outside end of the side track, where they cross the roads and ropes and continue between the empty trip and the other rib until they come to the head end of this trip. They are then hitched to the cars and proceed to make another trip to butt headings.

The engineer always stops when a trip of cars is near this sidetrack unless he is belled to pass without stopping, which is generally done. As the party who signals the engineer stands where the mules cross the tracks, there can be no danger to the mules even though they are unattended. The side track has been in use for over one year, and no accident of any kind has occurred. Empty trips pass in and loaded ones out, while drivers place cars on the loaded track and take empties away. The cars and mules never interfere with the ropes, which continue to end side track without deflection.

Before this intermediate side track was put in by the writer, a local hoist was used to haul loads from end side track to rope, as the grade was too great for mule haulage. The grade was also such that the empties would not take the rope in with them. This necessitated a mule and driver to place the empties on inside turnout. The hoist, engineer, driver, and mule are now not needed; the outside haulage engine does all the work.

Although conditions were especially favorable for this style of side track there is no doubt but that it could be used to advantage elsewhere where considerable coal must be put on the rope at intermediate points. In grading next the bridge, care must be taken that the grade is kept under the maximum on the haul. As will be seen by referring to figure, the empty and the loaded track are cut down in solid rock near crossing, while the main track is raised. In this way sufficient height is gained for the mules and cars to pass under the bridge. Large T iron rails are used on the bridge, and 4-inch oak plank laid alongside of them. Two 2-inch cross-planks are bolted to the 4-inch plank, and center posts placed under them as shown. Regular bents of square timber are at the ends of the bridge.

This side track is quite as simple in operation as the ordinary end tail-rope side track—in fact, more so, as the ropes do not interfere with the mules. The side track holds one trip, or 16 to 24 cars, depending on the number ready. The output of the mine is 600 to 800 tons a day. The grade next the bridge should be somewhat less than the maximum grade on the haul, so as not to increase the stress in the tail-rope by putting in the bridge, either by pulling in empties or holding back loads. This haulage road is 4,500 feet long.

In the figure are shown the grades of tracks and measurements. The arrows indicate the direction the cars run on the several tracks, except in cases showing direction of pitch, where the amount is stated.

Correction.

In the April issue an error was made in the list of successful candidates at the mine foremen's examination in the Eleventh Bituminous District. First-grade mine foremen's certificates were granted to A. N. Price, Mt. Pleasant; Archibald Sneddon, Tarrs; Andrew Laing, Summit Mines; Allin S. Snyder, Summit Mines. It was erroneously stated that the above received certificates of the second grade.