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THE MANUFACTURE OF PORTLAND CEMENT.

Regarding the history of the manufacture of Portland cement, but little need be written. Most persons are somewhat familiar with this uninteresting part of the subject, and indeed, as the industry is yet in its infancy, it can hardly be said to have a history.

The principal characteristics which, in the process of manufacture, sharply and clearly distinguish Portland cement from Limes, Hydraulic Limes, and other Hydraulic cements, are the necessity for carefully proportioning and finely grinding the raw materials to insure a homogenous mixture, and the extremely high temperature at which it must be burned in order to insure a sound and trustworthy product. The use of lime and hydraulic lime in building operations is of great antiquity, but not until about the year 1757 was the important discovery made that the addition of small amounts of clay calcined with the limestone brought about an improvement of the product and produced a hydraulic lime, or a lime which, when made into a mortar, possessed the peculiar property of hardening to some extent under water. The nature of the change brought about by the addition of clay was not understood , and it was not until about the year 1824 that the makers discovered that if the temperature of calcination was carried to incipient vitrifactiona much superior product would usually result. But even then no attention was given to the chemical composition, and consequently the uncertainty in the character, and the utter unworthiness of some of the cement produced, brought the whole matter into disrepute in England, where the process was discovered. It was not until about 1852 that the study of the production of Portland cement was taken up in Germany, and in 1855 the first Portland cement works were erected near Stettin. There are now about one hundred and seventy works in Germany.

For some time it was thought that Portland cement could not be made in America, and all that was used was necessarily imported from abroad, mainly from Germany. The first works in this country were established at Coplay, near Allentown, Penn.,in 1875. For many years these and other works have struggled against an ignorant prejudice in favor of the foreign cements, but of late years this prejudice is rapidly disappearing, and deservedly so. A number of our manufacturers are now regularly producing an article equal if not superior to any foreign brand.

The following figures, taken from "The Eighteenth Annual Report of the Director of the United States Geological Survey, 1896-97, Mineral Resources of the United States, Calendar year 1896; Nonmetallic Products," are given to show the growth of the Portland cement industry in the United States. (The probable production for 1875 was 1700 barrels.)

	1890		1894		1896	
	No. of works	Product barrels	No. of works	Product barrels	No. of works	Product barrels
New York	4	65,000	4	117,275	7	260,787
Lehigh Co. Pa. Phillipsburg,N.J	5	201,000	7	485,329	8	1,048,154
Ohio.	2	22,000	4	80,653	4	153,082
All other sections	5	47,500	9	115,500	7	81,000
Total	16	335,500	24	798,757	26	1,543,023

The imports, in barrels of 380 lbs. net, of Portland cement into the United States in 1895 and 1896 was 2,997,395 and 2,989,597 barrels respectively.

It is now perfectly well known that suitable mixtures of carbonate of lime and the constituents of clay can be prepared from raw materials to be found in all parts of the world, and the resultant product depends more upon the method of preparing the raw ~~material~~ mixture, and of carrying out the subsequent processes of manufacture, than upon the raw material, supposing of course that they are at all suitable for making a Portland cement

Careful experiments have proved that the only essential constituents of a cement are lime, silica, and alumina; but there are numerous other ingredients which are always present in Portland, some of them being beneficial, some being inert or merely replacing essential components, and finally, certain others which are undoubtedly injurious, except when present in very small percentages. The color of Portland is probably due entirely to the iron which is always present, generally in the form of the lower oxides. It may be inert, or at best may combine with the aluminate of lime to form an alumino-ferrite of lime, which is beleived by some writers to aid in the crystallisation of the calcium silicate. M. Le Chatelier assigns to it the formula $2(Al\ Fe)_2O_3\ 3\ CaO$. Iron may be helpful by acting as a flux during the burning, but cannot be regarded as an essential.

The alkalies, soda and potash, are nearly always present, being derived from the clays or clay shales, and are regarded by some chemists as being helpful during the process of calcination by acting as carriers of the silicic acid to the lime,. They are not essential.

Magnesia is nearly always present in quantities varying from 1% to 3%. It is probably present in hard-burned cements in the free state, and is regarded as dangerous to the cement when the amount is much greater than 4%. This danger arises from the fact that magnesia in becoming hydrated increases very considerably in volume, and as this ~~increase~~ process of hydration goes on very slowly, the swelling does not take place until long after the cement has become hard set. Dr. Erdmenger found that in some cases cements were disintegrated by the hydration of their contained magnesia after remaining sound for almost two years.

Sulphur, in excess, is certainly injurious, although a definite limit cannot be given which would apply to all cements alike. The beneficial effect of adding small quantities of calcium sulphate to the finished Portland is recognised by all manufacturers, and the practice of adding small amounts, up to about three per cent, is probably a universal one. By this means it becomes possible to control the rate of setting of a freshly made cement, trifling additions of the sulphate making the setting slower and slower, besides greatly augmenting the tensile strength, both when tested neat and when tested with sand. A gain of 25% to 30% in tensile tests is not uncommon bt such addition. A cement high in alumina and burned at a low temperature will bear a larger addition of the sulphate than one low in alumina and burned at a higher temperature. Spalding says that an addition of 10% might not be injurious to a highly aluminous cement.

Water and carbonic acid, if present in any considerable proportion, indicates that the cement must be very old, or that it was not properly calcined. A freshly burned Portland should show an ignition loss less than one-half of one per cent.

In the following description of the processes employed in the manufacture of Portland cement the writer will adhere very closely to the methods employed by one of the foremost manufacturers of this region. The manufacture may be divided into three principal divisions as follows;

1st, grinding and mixing together the carbonate of lime and the clay to form the raw mixture, 2nd, burning the mixture, and 3rd, grinding the resulting clinker to a fine powder.

The materials used here are, a cement rock, which is essentially a limestone containing such an amount of clay as to be approximately a natural Portland cement mixture, and a limestone containing from 88 to 95 per cent of carbonate of lime, which is added to the cement rock in quantities sufficient to bring the mixture to the desired composition. Both of these materials are about as hard as ordinary limestone used for building purposes, and this naturally points to the "Dry Process" as the best method for their reduction

Naturally the different strata of cement rock varies considerably in chemical composition, as does samples taken from the same stratum. For any given materials there is doubtless a definite chemical composition which will give the best possible cement from that material, and the raw mixture cannot vary by so much as one per cent from this without showing a noticeable deterioration in the product. This inevitable variation in the raw material gives rise to the necessity for a chemist, and no cement works is now considered complete without a well equipped laboratory. The general practice is to maintain a certain percentage of carbonate of lime in the raw mixture, as this is more easily determined by a partial analysis, and at the same time gives a good indication of the correctness of the mixture. The writers practice has been to make the partial analysis of both the cement rock and the limestone, taking samples of the drillings which are made ~~xx~~ preparatory to blasting out the rock. In this way the chemist is ready to indicate the weight of each which is to be taken for each charge sent to the grinding mill, by the time the rock is blasted loose in the quarries.

Various methods have been used for determining the percentage of $CaCO_3$ present in a sample of rock. Scheiblers Calcimeter has been widely used but is not satisfactory. Probably the best method is the volumetric one in which an acid is used to break up the carbonate, an alkali to neutralize the excess of acid used, and a coloring matter as an indicator. With this method a chemist can easily weigh a sample and make the determination in from six to ten minutes. These partial analyses are supplemented by an occasional complete analysis of both the raw materials and the finished cement.

After being properly proportioned the mixed limestone and cement rock is sent to the crushing room to be ground. The first step in the reduction is preferably performed by a Gates Rock-breaker. Common sizes of this machine are capable of taking the stone as they come from the quarry and reducing them to pieces not larger than a two-inch cube at the rate of from thirty to fifty tons per hour. The broken stone is now passed through a Dryer which drives off all moisture and makes the subsequent grinding much easier. The dryer is a cylindrical shell resting on friction rollers, and having its axis on a slope of about one-half inch per foot from the horizontal. The shell is about thirty feet long and four feet in diameter, and is made of three-eighth inch steel. It is revolved by means of a large spur gear around the outside of the shell, and makes about one revolution per minute. Both ends of the shell are open, the lower end connected with a furnace, the upper end being connected with the smokestack. It is heated by means of a coal fire in the furnace. The broken stone is fed into the upper end and by the revolution of the dryer is passed through the hot gases and gradually carried to the lower end, where it is discharged into an elevator and carried to mills which give it a further step toward its final reduction.

A mill in common use for this work is the Mosser Crusher, which is something like a coffee-mill in principle, and reduces the stone to pieces not larger than a one-half inch cube. Crushing Rolls are also coming into quite extensive use for this reduction. The material is next conveyed to a third set of mills where the final reduction to a fine powder is made. The most common mill for this purpose is the Griffin mill. The outlet from these mills is through fine brass wire screen, thus preventing any coarse particles escaping reduction. In a general way, the finer the raw material is ground the better the resulting cement. In practice the increased cost of reduction limits the fineness to which the grinding is carried. The best results cannot be obtained if the raw material, after leaving the finishing mills, shows a residue of more than 12% or 15% on a standard sieve containing 10,000 holes per square inch.

By this method of grinding the limestone and cement rock together from the time they enter the crushing room, the raw mixture becomes practically homogeneous, which is an absolute essential in the manufacture of Portland cement.

From the finishing mills the raw mixture is conveyed to the burning romm, which is perhaps the most interesting and at the same time the most important step in the process of manufacture. The most improved system of burning is by means of the Rotary cylinder, similar in arrangement to the cylinder used for drying the stone. The size of the cylinder is varied by different manufacturers. They are commonly about 60' in length and 6' in diameter for a distance of 25' at the furnace end, then a section about 10' long in which the diameter is reduced to 5', and then a second straight section 25' long and 5' in diameter. The enlarged end of the cylinder gives additional heating surface at the point where the temperature is highest, and will consequently burn more cement than the straight cylinder 5' in diameter. Experience does not seem to warrant the making of cylinders larger than 6', although there are a few in use that are 7' in diameter.

These Rotary cylinders are heated by a jet of crude petroleum oil or finely powdered coal, which is blown into the cylinder by means of compressed air. The raw material in the form of a dry, impalpable powder, is fed into the upper end of the cylinder, which, by its rotary motion, passes and repasses the powder through the hot flame and gradually carries it to the lower end, where it falls out into cooling bins in the form of hard, well sintered lumps, to which the name of"clinker" has been given.

The temperature at the upper end of the cylinder may be about 540 degrees C. (1000 degrees F.), and this gradually increases until it reaches a maximum at about 10' to 15' from the lowerend, where it is about 1375 degrees C. (2500 degrees F.) to 1660 degrees C. (3000 degrees F.). As the raw material is exposed to this heat chemical action begins by the expulsion of the carbonic acid gas, which probably begins as soon as the mixture enters the cylinder. The lime is now left in what is termed the nascent state, and is ready to form new combinations, with the silica and alumina of the clay. The alumina, which is usually regarded as a base, assumes at very high temperatures acid functions, and here combines with the lime to form the dicalcium-aluminate, $2CaO,\overset{Al_2O_3}{\cancel{SiO_2}}$. The silica combines with the lime to form the tri-calcic silicate, $3CaO,SiO_2$. Iron and magnesia probably remain inert, or at least have but little influence on the chemical changes taking place, and according to the best writers, should not be considered in proportioning the charge of raw materials.

If the charge has been correctly proportioned and finely ground, and the burning properly carried out, the clinker comes from the cylinder in dense, heavy, black or greenish-black lumps, which when exposed to the light, are seen to be covered with sparkling crystals. These lumps are sufficiently hard to scratch glass and undergo no alteration when exposed to the air. Indeed, one case is cited in which Portland cement clinker remained unaltered by being immersed in sea-water for five years.

If the grinding has been coarse, no amount of careful burning can produce good clinker. The color will usually be dead and lustreless, while some lumps may be of a faint violet, purple, or pink tint, interspersed with whitish particles. Such clinker when ground produces a weak cement which will not show sound in the hot water or steam pat test, owing to the lime which is inevitably left free if the mixture be not perfectly homogeneous.

It is commonly stated by persons writing on this subject, that great care must be exercised in burning Portland in order not to overburn it, thereby producing a heavy cement, but one which will not set when mixed with water. Experiments made by the writer to determine the effect of the so-called overburning would seem to point to the conclusion that it is practically impossible to overburn a cement of correct chemical composition, or one that has sufficient lime to form the tri-calcic silicate and the di-calcic aluminate. Such a mixture when burned until the resulting clinker resembled blast furnace slag in appearance, was only slightly slower in setting than when burned at the normal temperature, and remained in all tests to which it was subjected, as sound as the normally burned clinker. However, if the mixture be low in lime, so that the ortho-silicate, $2CaO.SiO_2$, is formed, andis burned to the point of fusion, it gives rise to the peculiar product known as "creeping" clinker. When this silicate is fused and allowed to cool slowly, it crumbles to a powder resembling slaked lime in appearance and composed of fragments of minute twinned crystals. This action is due to the unequal tension on the opposite faces of the crystals. If the compound is burned at a lower temperature the twins are not formed and no disruption takes place. This action of the lower lime mixture has no doubt given rise to the supposition that all mixtures are ruined by overburning. In general , the lower the lime content of a raw mixture the lower must be the maximum temperature at which it is burned, and the quicker the setting of the resulting cement.

As the clinker falls from the cylinder it is carried away by a conveyor and stored in bins, or spread on a floor to be cooled before grinding. As it comes from the cylinder the clinker is very tough and difficult to grind, but if left until it is thoroughly cooled it becomes brittle and is much easier to pulverize. There are a number of different mills in use for pulverizing Portland cement clinker which give fairly good results. Among the best are the "Ball mills", which do the preliminary crushing by means of a number of steel balls within a revolving drum into which the clinker is fed, the clinker being pounded to a coarse powder before it can leave the mill; and the "Tube mills", which do the finishing by means of the rubbing action of flint pebbled within a revolving cylinder into which the crushed clinker is fed. The fineness to which the cement is ground is controlled by the rate of feeding the mill, and requires no screening or bolting. The cement is now a finished product, but usually requires a few days for aeration and seasoning before it is really fit for use. An addition of calcined plaster, or sulphate of lime, to the ground cement helps to obviate the necessity for aeration, and is usually resorted to by the manufacturer. Such addition is a legitimate part of the process of manufacture, and should not be regarded as an adulteration of the cement.

It is of common occurrence for Engineer's specifications to require that "all cement used must be freshly ground Portland, etc," According to the writers belief this is not a desirable requirement and should probably be reversed to obtain the best results. Many cements which when freshly ground would fail in the test for soundness, will, after being exposed in the storage bin for two or three weeks or longer, become perfectly sound, and are safe to use in any work. It is probable that Portland cement does not deteriorate, even when kept for many months, if well protected from moisture.

Engineers frequently make the test for tensile strength of the neat cement the test upon which it must stand or fall, while not imposing a severe requirement as to fineness of grinding. The neat test should be given a second place in testing Portland cements, making the tensile strength of a 1 : 3 sand mixture the important requirement in this direction, ~~for the~~ following reasons; The strength of a neat cement mixture gives little or no idea of its sand carrying capacity, and as nearly all Portland cement is used only when mixed with sand, this becomes the test of practical importance. A cement which when rather coarsely ground would just reach a certain requirement as to tensile strength, might be condemned if very finely ground; yet the finely ground cement would in all probability show as great strength when mixed with three parts sand as the same cement coarsely ground would show when mixed with only two parts sand. A slight addition of sand will increase the tensile strength of a very finely ground cement. It therefore becomes evident that fine grinding is an important requirement for Portland cement, the practical limit being reached when the increased cost due to fine grinding balances the gain from its greater sand carrying capacity. A limit of 20% or 25% residue on a standard sieve having 200 wires per lineal inch, or 40,000 holes per square inch, is not a too severe requirement where a first-class cement is expected.

Allentown, Penn., May 25th, 1898.

Herman A. Cowen,