HYDRAULIC CEMENTS.

THE following instructive paper, by Mr. Edward F. Ball, was read before the members of the Toronto Architectural Sketch Club, at their meeting on the 4th inst :

MR. PRESIDENT AND GENTLEMEN,—It is a popular belief that the cements used by the ancient Romans in the construction of their roads, aqueducts and other public works was superior to any in use at the present time, and that the process of its manufacture is a lost art. It may seem somewhat startling, however, to state the fact that with all the advantages they have had in hardening slowly from two to three thousand years, probably none of them is equal in strength to good Portland cement mortar made of one part cement and two parts sand *one week old*. On the shores of the Bay of Naples cement is made and used at the present day in substantially the same manner as described 2000 years ago by the old architect Vitruvius.

In remote antiquity, before the Roman era, the builders of ancient cities all over the world depended for strength and durability upon the extreme accuracy with which they dressed the surfaces of the large stones which were to be placed in contact, and also upon the bronze dowels used in uniting them. With the Romans, beside accurate stone cutting, two kinds of mortar were used. In situations where it would not be exposed to the dissolving action of the water carefully prepared lime mortar was employed, while for quay walls, aqueducts, drains, cisterns, etc., hydraulic cement was used. As is well known, ordinary lime mortar will not set under water, but if lime be mixed with clay and burned at a high temperature, a substance is formed which sets and continues to harden indefinitely, even when immersed.

The purest limes, sometimes called rich or fat limes, when freshly burned combine readily with water, which process is termed slaking. In so doing they expand, evolve great heat, and fall to powder.

Impure limes, sometimes called poor limes, do not slake so readily.

Hydraulic limes, containing a considerable quantity of clay, scarcely slake at all, and possess the property of hardening under water.

Hydraulic cements do not slake at all, and will set and harden under water.

The particles of lime have greater adhesive than cohesive force, *i. e.*, they will adhere to other substances more strongly than to each other. In hardening, mortar made from lime alone changes volume, and for these two reasons, as well as for economy, sand is used in all mortar made from lime. Good hydraulic cement does not change its volume in setting or hardening, and its cohesive strength is greater than its adhesive, so that sand is used with cement simply for economy.

Cements are divided into two classes, Portland and Natural or Rosendale.

Portland cement was first invented or discovered in 1824 by Mr. Aspdin, of Leeds, England, while experimenting with some of the over-burned clinkers of artificial cement which was then being manufactured. After pulverizing and wetting up into cakes or blocks, it became very hard and in color resembled a limestone that was being quarried for building purposes on the Isle of Portland. In taking out a patent for the new product it was named "Portland." In certain localities natural deposits of rock are found, from which Portland cement may be manufactured, but fully nineteen-twentieths of the Portland used in the United States is artificial. It is made by thoroughly mixing together in suitable proportions clay and finely pulverized carbonate of lime (either chalk, marl, or compact limestone), burning the mixture in kilns at a high temperature, and then grinding the burnt product to fine powder between ordinary millstones. In England the ingredients of the cement are mixed together with a large quantity of water and afterwards dried, burned and ground. This is called the wet process. In Germany the ingredients are mixed dry. It is very important that the ingredients be correctly proportioned, finely ground and thoroughly mixed. No substance coarser than the one-thirtieth of an inch will make cement, and the finer the ingredients are ground the better. Thorough mixing is even more important than correct proportioning, as the temperature in the kiln is not allowed to rise high enough to liquify the mass, and in order that the chemical changes may take place, the particles of lime and clay must be in close contact with each other, otherwise uncombined or "free" lime or clay will be left. In the wet way of mixing, the chalk and clay being of different specific gravities, are liable to become deposited irregularly, even under the most careful supervision. In the dry method, when the water necessary to form the mass into bricks is added, the ingredients are liable to become separated unless the water is added carefully. The first chemical change which occurs in burning is the expulsion of chemically combined water and carbon dioxide; thus calcium carbonate Ca C O_3 is converted into lime Ca O. The silica Si O_2 which is present as silicate of alumina in the clay, is partly transferred to the lime, forming a double silicate of lime and alumina. A high temperature is necessary for the production of this double silicate, but at a lower temperature the alumina which was present in the clay as a base plays the part of an acid, and combining with the lime, forms a tri-calcium aluminate, $Ca_3 Al_2 O_6$, or as it may be written $Al_2 O_3$ 3Ca O. If the temperature be too high, a lime glass is formed which has no hydraulic properties, and if the burning be continued at this temperature, a solid crystallization between the silicate and aluminates of lime is formed, which does not set.

SETTING OF CEMENT.

The setting of cement is a complex process, partly chemical, partly mechanical. The chemical reactions give use to substances which as soon as formed combine with water and constitute the true cementaceous material. The tri-calcium aluminate $Ca_3 Al_2 O_6$ is soluble in 3000 parts of water, and in the act of setting first dissolves and then begins to separate as a mass of felted needles, consisting of calcium aluminum hydrate, which extend in every direction and are directly the cause of the first setting of the cement. At the same time an action begins which requires a much longer time for its completion, and which probably consists in a combination of the first formed aluminium hydrate with the tri-calcium aluminate and the water forming a mineral of the probable composition $H_{10} Ca Al_2 Si_4 O_{17}$. This substance crystallizes out as it forms, and this continues to add to the solidity and tenacity of the cement for long periods subsequent to the first setting. Some experiments made by the writer seem to confirm the theory that aluminium plays an important part in the first setting of the cement, and also that this is dependent in a measure upon the solubility of some of the ingredients. The experiments are as follows: Aluminium, in the form of alum (either raw or burned) added to cement and moistened, causes the mass to rise greatly in temperature, showing that a chemical change is taking place, probably the formation of tri-calcium aluminate before referred to; a sample of Improved Union cement mixed neat with water, set in 20 minutes; a sample of the same cement with two per cent. of burnt alum added, set in 8 minutes; same with 4 per cent., set in 7 minutes; same with 6 per cent., set in 7 minutes. A solution of aluminium hydrate in caustic potash produced the same effects, but in a less marked degree. It is a well known fact among cement testers that in order to get the full strength of the cement it must be thoroughly mixed and kneaded or stirred after the water has been added. This seems to indicate the presence of a soluble constituent which it is necessary to diffuse throughout the mass in order to obtain the maximum strength. If dry cement be forced into moulds under a pressure of say 70 lbs. per sq. inch, and then allowed to absorb water, a very dense, hard briquette will be formed, but it will be very weak in strength, and also very uncertain. If sufficient water be added to dry cement to properly moisten it, and if the mass be stirred just sufficiently to ensure thorough and complete moistening, and the briquette put into the moulds in the usual way, it will not be so dense or compact as if made in the way described, but will be much stronger. If, instead of slightly stirring the moistened cement, it be thoroughly turned and kneaded as long as possible before setting begins, the best and strongest briquette may be made. All this, in the opinion of the writer, points to the existence of a soluble constituent as before remarked.

IMPURITIES.

If by reason of imperfect proportioning, grinding or mixing, any portion of the lime fails to combine chemically with the silica or alumina of the clay, this is known as "free lime," and when the cement is fresh, is in the form of CaO. Upon exposure to the air it absorbs moisture and becomes slaked, thus: $CaO + H_2O = Ca(OH)_2$. Upon still further exposure it slowly absorbs carbon dioxide, and returns to its original composition before being burnt, viz., carbonate of lime: $Ca(OH)_2 + CO_2 = Ca CO_3 + H_2O$. When present in the unslaked form, (Ca O), free lime is one of the most dangerous impurities in cement, as upon the addition of water it slakes and expands, thereby disturbing the setting of the cement. This slaking is not rapid like that of rich or fat limes, and often its effects are not apparent for the first day. It frequently happens that samples of cement will stand a good tensile strain at the end of 24 hours, while at the end of seven days the strength will hardly be greater than the 24 hours test—sometimes even below it. This generally indicates free lime, and in such a case the sample should be exposed to the air for a week and a second test made. If this test comes up to the standard, the trouble is due to the presence of free lime, and the cement may be accepted provided the other tests are satisfactory, on condition that it be spread out and exposed to the air for a week or more before use. If the lime have sufficient activity, thin cakes of the cement immersed in water for a week will become cracked, but if the lime is not present in sufficient quantity or has not the necessary activity, no cracks may appear. In order to render this test more effective, the cakes or pats may be exposed as soon as they are hard to a high temperature saturated with moisture for about three hours, and then boiled for twenty-four hours. Two per cent. should be the limit of this impurity, especially if the cement be for use under water; for use in air the presence of free lime is not so injurious, provided, of course, that it is slaked. Free lime retards the setting of cement and impairs its hydraulicity. When present in considerable quantity the cement will disintegrate on immersion, unless first allowed to become quite hard in air. In determining the amount of free lime in cement by chemical analysis, it is customary to find the amount of C O_2 on the supposition that the free lime is all in the form of carbonate, and then calculate the amount of Ca O – 1 per cent. of C O_2, indicating 1.3 per cent. of Ca O. This, however, is a very unreliable method, as the lime must first be hydrated and then carbonated. This requires a long time if exposure to the air is relied upon to effect the change, as is usually the case. Hydrogen Sulphide, H_2S, is often evolved with the carbon dioxide, and this also affects the accuracy of the test.

Magnesia (in the free state) is another dangerous impurity. It may not prevent the cement from setting and becoming apparently as hard as though it were absent. For a long time it may remain inert, and perhaps for months there may be no apparent change. The magnesia, however, has an affinity for water; every two pounds of magnesia in becoming hydrated, takes up and solidifies one pound or 27 7 cubic inches of water, and in bulk every ton of magnesia would have to find room for about 16 cubic feet of water. In finding room for this water the mortar becomes disintegrated. The action continues whether in air or in water, and is especially disastrous in concrete work. Instances are recorded where concrete works have failed although built in the usual manner with cement that had stood the ordinary mechanical tests. The concrete set as hard as usual, but after a time expansion set in. In one case, a vertical wall about 35 feet high was lifted about 2½ inches, in another, a mass of concrete 16 feet thick was lifted from ½ to 1¼ inches. In both cases a white substance of the consistency of cream was seen in the concrete. On being analyzed, this substance was found to contain 80 per cent. of magnesian hydrate, consisting of about ¾ magnesian oxide and ¼ water. The writer made some experiments with five per cent. by weight of calcined magnesia added to Improved Union cement. The magnesia was found to render the paste very plastic and easily worked. It retarded the setting from twenty minutes to two hours, and greatly decreased the strength of the cement, as follows:

Neat cement, 1 day old, tens. strength	= 45 lbs. per square inch.	
" " 1 week old, " "	= 74	" "
Cement with 5% mag., 1 day old, tens. strength,	= 1	" "
" " " 1 week old, " "	= 19	" "
" " " 2 " "	= 36	" "

At the end of one week the pats were very soft; the outside was light-grey and the interior the usual color. Good Portland cement should in no case contain more than one per cent. of magnesia.

By the rules of the "Ecole Nationale" of Paris, if the amount of sulphuric acid exceeds 1½ per cent., the cement is rejected on the chemical analysis alone.

When Portland cement is properly burned, it forms a very hard clinker, which is expensive to grind to the fineness now demanded by engineers, as the machinery requires constant repair. To render the grinding easier, iron slag meal is sometimes added to the cement clinker. This slag cement may be recognized by its lighter specific gravity (2.60) and by its color, which is a mauve tint in powder, while the inside of the water pat when broken is deep indigo. Its presence when mixed with Portland may be detected as follows: To a gill of water, add about 80 drops of sulphuric acid. Into this drop 25 grains of the cement and stir rapidly with a glass rod, and while still stirring, pour in drop by drop, a solution of Condy's fluid (64 grains of permanganate of potash to one pint of water) until the red color remains permanent. Genuine Portland will require only 10 to 15 drops of the permanganate solution, whilst an adulterated cement will take considerably more—30 to 60—and a cement made from slag over 200 drops. The principle of this test is as follows: Solid permanganate of potash is at once decomposed by the addition of strong acids, but in water solution this decomposition does not at once take place except by contact with oxidizable substances. This action is apparent by the change of color, the deep purple being rendered colorless. All Portland cements contain a small quantity of iron; thus with unadulterated cements a certain amount of the permanganate will be bleached, but cements containing iron in undue proportions will bleach a much greater quantity of the solution. A simple test for the same purpose is as follows: Place upon a clean silver coin a thin layer of cement, and drop on it a small quantity of dilute sulphuric acid (one acid to seven water) and afterwards rinse with water. If the cement be genuine Portland, the treatment will only slightly affect the color of the silver, but if slag be present in any notable proportion, a dark brown stain will be produced. Slag cement has been for some time manufactured in Germany, and works