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Cement

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CEMENT.

BY FRANK L. CULIN, JR.

"A cement is any compound which, under certain conditions, is plastic, and under others develops tenacity, and can be used for holding together various materials." By far the most important, structurally and commercially, are the hydraulic cements, compounds of lime, silica, and alumina that have the property, when mixed with water to a paste, of cohering or setting, and finally becoming stone hard, even under water.

There are four general classes of structural cement: (1) hydraulic lime; (2) hydraulic or natural rock cement; (3) Portland cement; (4) Puzzolan or slag cement.

Of these four types, Portland cement is the most important. Large quantities of natural-rock cement and hydraulic lime were formerly used, but since the introduction of Portland cement, the production of these two types has been steadily and rapidly diminishing. Puzzolan cement is much used for certain classes of work, and the manufacture of this type is a promising industry. Hydraulic lime has never been made in this country, due to the excellence of the natural cement, and the abundance of Portland cement materials.

Until the introduction of Portland cement, natural rock cement was the type most used in the United States. Portland cement was first made in England in 1824. It takes its name from Portland Island, in the English Channel. The industry was later taken up in Germany and other countries, and has grown enormously. Portland cement was first made in the United States at Coplay, Pa., in 1878. Although many plants were established, the output was small until after the middle nineties. Since then the industry has developed rapidly, until it is now one of the most important in the country.

Slag cement was first used by the ancient Romans, who made it by mixing slaked lime with volcanic scoria, or "pozzuolana," whence the name. Its durability is attested by the condition of many ruins. In this country the industry did not exist until 1895. The maximum output of this cement was in 1907; it then fell off very considerably, but is again increasing, though not to its former mark.

CEMENT MATERIALS

Silicate of lime or magnesia are the main components of hydraulic cements of all kinds. All hydraulic cements, as the name implies, require water for setting.

Other materials used in cements vary according to the class. Puzzolan cements use either volcanic rocks, containing soluble or hydrous

silicic acid, or slags. Natural cements are a natural mixture of limestone and clayey material. Portland cement is an artificial mixture of limestone and clayey material.

RAW MATERIAL FOR PUZZOLAN CEMENT

Puzzolan cements may be divided into two classes—natural and artificial.

Natural puzzolan is a mixture of puzzolan proper, trass, or san-torin earth, and slaked lime. Puzzolan proper is hydrous, volcanic, porous rock found in Italy. Trass is also a kind of volcanic tufa, being consolidated volcanic dust which has been subjected to the action of pressure and water. Santorin earth is a kind of volcanic material, resembling pumice stone.

Artificial puzzolans are slags and de-hydrated clays. The slags used for this purpose are the waste products of blast furnaces smelting iron from its ores.

RAW MATERIALS FOR NATURAL CEMENT

This is a natural intimate mixture of calcium carbonate and clay. The amount of clay present in the limestone varies considerably, from 20 to 50 per cent.

CLAY MATERIALS USED FOR PORTLAND CEMENT

"Clay may be defined as a complex derivative rock, generally of a soft and earthy nature, in which a mass of mineral debris of variable composition and amount is bonded and held together by a matrix of kaolin or allied hydrous silicates of aluminum. The distinguishing characteristics of clays as a class are—first, plasticity when ground and mixed with a sufficient amount of water; and second, the property of hardening by heat to form strong and durable silicates."*

Clay, since it is a derivative rock, has a variable composition. Pure clay is a mineral called kaolin. The clays used in ordinary cement manufacturing, however, are impure, and may contain any or all of the following substances—silica (as quartz), feldspar, iron oxide, mica and other iron bearing minerals, gypsum, calcite, dolomite, rock fragments, and various other impurities.

Quartz is usually a detriment to cement clay, for the reason that it must be in a very finely divided state before it will be available for chemical combination, the limiting diameter being close to 0.0003 inch. To reduce quartz to this size means an excessive grinding expense.

* A. V. Bleining, I. S. G. S. Bull. No. 17.

The presence of feldspar in clay is desirable up to a certain limit. The silica in feldspars is in a combined state, and therefore readily available for combination with the lime of cement mixtures. The limiting factor is the alkali content—since this must not become too high.

Iron oxide (ferric state), is an exceedingly important constituent of cement clays, since it lowers the vitrification temperature of the clay. In order to be of maximum benefit, the ferric oxide should be very finely divided and in a colloidal condition.

Mica is always present in clays. Other iron-bearing minerals are augite, hornblende, and occasionally, magnetite. Since the silica in these minerals is in combined state, they are an aid to the formation of the silicates necessary for the cement reaction.

The principal physical characteristics of clay to be used for cement are: fineness of grain, hardness, density and uniformity. A clay possessing a fine grained structure materially reduces the cost of grinding. There is also a more intimate contact established between the grains of clay and the more numerous particles of limestone. A clay should not be excessively hard. This applies only to very hard and partially metamorphosed materials similar to slate. Ordinary shales may be satisfactorily used.

The superficial area of the total number of grains in a unit weight of clay should be as great as possible. Therefore, a dense clay is not as desirable as a lighter, fine-grained one. However, a dense clay makes a greater weight of cement by volume, and as cement is sold by weight, this is a consideration in favor of the heavier clay. It is self-evident that uniformity is desirable.

LIMESTONE MATERIALS FOR PORTLAND CEMENT

The lime bearing materials may be limestone, marl, slag or industrial waste products. Limestone and marl are the principal materials.

The limestone most used is of two types: (1) Dense, dull, hard, impure stone, and (2) calcareous shale rock. These rocks are desirable because they contain the required clay matter, either wholly or in part, and in a very desirable condition, being finely disseminated and blended with the carbonate of lime. If such material is not to be had, the pure crystalline or granular limestone is used.

MINERALS

The most important minerals of cement materials are calcite, kaolin and feldspar, the two latter named being constituents of clay.

CALCITE

Chemical Composition: Calcium carbonate (CaCO_3). Carbon dioxide (CO_2)=44.10; lime (CaO)=56.0; 100%. Small quantities of magnesium, iron, manganese, zinc and lead may be present replacing the calcium.

Form: Pure varieties usually crystalline, crystallizing in the rhombohedral division; also fibrous, both coarse and fine; sometimes lamellar; often granular; from coarse to impalpable, and compact to earthy.

Color: Variable—from clear to colorless through yellow, pink, purple, blue to brown and black.

Streak: White or grayish.

Hardness: Rather soft in crystalline varieties. (3). Earthy varieties softer.

Weight: Pure crystals are light (Sp. Gr. 2.7), but weight varies according to impurities present.

Occurrence:

1. Beds of limestone.
2. Veins.
3. In cavities and veins of igneous rocks.
4. Near hot springs.

Blowpipe Tests: Before blowpipe infusible; colors the flame reddish yellow; after ignition, reacts alkaline. Strong effervescence with hydrochloric acid; completely soluble in hydrochloric acid.

KAOLIN

Chemical Composition: A hydrous aluminum silicate, having the formula, $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$, or $2\text{H}_2\text{O}$, Al_2O_3 2 SiO_2 =silica (SiO_2) 46.5%, alumina (Al_2O_3) 39.5%; water, (H_2O) 14.0%; 100%.

Form: Usually constitutes a clay-like mass, either compact, friable or mealy.

Color: White, grayish white, yellowish, sometimes brownish, bluish, or reddish.

Hardness: very soft (2-2.5).

Weight: Light. Sp. Gr. 2.6 to 2.63.

Occurrence: Usually in beds, resulting from decomposition of aluminous materials, especially the feldspar of granitic and gneissoid rocks and porphyries.

Blowpipe Tests: Before blowpipe infusible, but yields water. Gives a blue color with cobalt solution. Insoluble in acids. Characterized by an unctuous soapy feel.

FELDSPAR

The name feldspar applies to a group of minerals, in general silicates of potassium, sodium and aluminum. For the purposes of this bulletin it will be sufficient to describe just the potassium aluminum feldspar, called orthoclase.

Chemical Composition: A silicate of potassium and aluminum, $KAlSi_3O_8$ or $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ = silica (SiO_2) 64.7; alumina, (Al_2O_3) 18.4; potash (K_2O) 16.9=100%. Sodium is often present, replacing part of the potassium.

Form: Usually crystalline, monoclinic system. Often massive, coarse, cleavable to granular; sometimes lamellar. Also compact, and flint or jasper-like.

Color: Colorless, white, pale yellow and flesh red common, gray, rarely green.

Streak: Colorless.

Hardness: Moderately hard, can be scratched by a knife. (H=6). Harder than calcite.

Weight: Light. Sp. Gr. 2.57.

Occurrence: An essential constituent of crystalline rocks, as granite, gneiss, syenite, porphyry, trachyte, phonolite, etc. In the massive granitoid rocks it is seldom in distinct, well-formed crystals, except in veins and cavities. Crystals well developed in pegmatites.

Blowpipe Tests: Before blowpipe fuses at 5 (difficult). Not acted upon by acids. Characterized by crystalline form and two cleavages at right angles to each other.

THE CHEMICAL AND PHYSICAL EXAMINATION OF CEMENT
MATERIALS*

Prospecting and Sampling: "In investigating a new property for cement raw materials, it must be realized that the best methods of examination are of no value whatever unless the samples analyzed represent truly the character of the deposit. The guiding principle should invariably be that the less homogeneous a deposit is, the more samples must be taken and the more carefully the work must be done."

"In looking for a suitable clay material the experienced prospector makes use of all natural and artificial excavations, such as gullies,

*From Bleninger, G. S. of Ohio, *Manufacture of Hydraulic Cements*. 1904; and I. S. G. S. Bull. No. 17.

river banks, railroad cuts, and quarries, for determining the character of the rocks in a certain locality. If a random sample of a clay outcrop has shown a satisfactory composition and is promising in regard to its physical characteristics, an opening should be made into it, removing the surface clay, and a sample taken from the material within the bank. If this should likewise prove satisfactory, the bed is attacked at several places, examined, and finally a survey is made of a tract which affords enough material for the capacity of the factory which it is intended to erect. The area of the land is plotted and a topographical survey made. Now the map is divided into squares, whose sides range between 50 and 100 feet in length, depending on the thickness of the deposit. At the centre of every square a test hole is sunk, and the material brought up by the drill is put aside for analysis." Samples are usually taken every five to ten feet, but this depends on the character of the ground.

The above method may seem a very tedious and unnecessary one, but when one considers the small cost of a good prospecting system, as compared with the enormous cost of a complete plant, the folly of not prospecting thoroughly may be readily seen.

Physical Tests: The simplest test of a clay consists in stirring a small amount of it in a glass of water, allowing it to settle a short time, decanting the liquid, and continuing this procedure until the water is clear. This shows in the glass an assortment of the various impurities in the clay. A further examination with a microscope or a good hand magnifying glass is of value for determining what these impurities are. This test also gives an idea of the fineness of grain of the clay.

The most important physical test of raw materials deals with the fineness of grain. This may be determined by: (1) separation by sieves; (2) sedimentation; (3) eleutriation; and (4) centrifugal action.

CHEMICAL EXAMINATION OF CEMENT MATERIALS

Puzzolan Materials: The hydraulic value of puzzolan materials depends on the amount of available or soluble silica present. A complete analysis is required in but few cases.

Furnace Slags: Furnace slags should be given an analysis for silica, alumina, calcium, magnesia, iron, and sulphur.

Natural and Portland Cements: Materials for these types of cement should be analyzed for silica, alumina, calcium, magnesia and iron.

For the purposes of this bulletin it is not thought necessary to embody a description of the methods of these analyses. They may be

obtained, however, from almost any standard work on cement materials, or from any good work on quantitative chemical analysis.

THE MANUFACTURE OF CEMENTS

1. *Puzzolan and Slag Cements:* Owing to the comparative unimportance of these types, little will be said regarding them.

The preparation of puzzolan cement is very simple and may be done in two ways: (1) Grinding of puzzolan rock together with calcium hydrate. (2) Grinding of puzzolan alone and mixing with slaked lime in the wet when used.

The slag used for cement manufacture is first determined by chemical analysis. It is granulated as it leaves the furnace either by a stream of water or by an air blast. If by water, it must then be dried. From the driers, the granulated slag goes to the intermediate grinding machines. It is then taken to bins for delivery to the fine grinding machines. At this state the hydrated lime is added.

A test of slag cement made at Youngstown, Ohio, gave the following results:

Silica	28.20%
Alumina and iron	11.60%
Lime	52.80%
Magnesia	2.37%
Volatile matter	2.75%
Sulphur	1.57%
Total	99.29%

It left approximately 3.8% on a 200-mesh sieve. The initial set was one hour and twenty minutes; the final set, three hours and ten minutes. It stood both the hot and cold tests for volume. The tensile strength is given in the following table:

TENSILE STRENGTH IN POUNDS PER SQUARE INCH

Age	Neat	1 cement; 3 sand
24 hours	330	75
7 days	502	223
14 days	610	310
21 days	545	322
28 days	715	348
3 months	655	340
6 months	728	340
1 year	758	343
2 years	768	408

2. *Natural Cement*: This branch of the cement industry is the simplest one, and consists solely in taking the rock as it comes from the quarry or mine, in lumps, burning it in plain upright kilns, and then grinding the burnt material to a powder.

The Amer. Soc. Civil Engineers suggest the following minimum and maximum tensile strengths per square inch for natural cements.

Neat Cement: One day; one hour, or until set, in air; the rest of the 24 hours in water, 40 to 80 pounds. One week; one day in air, six days in water, from 60 to 100 pounds. One month (28 days); one day in air, 27 days in water, from 100 to 150 pounds. One year; one day in air, the remainder in water, from 300 to 400 pounds.

Sand Mixtures: 1 cement; 1 sand, by weight. One week; 1 day in air, six days in water, 30 to 50 pounds. One month (28 days); one day in air, 27 days in water, 50 to 80 pounds. One year; one day in air, the remainder in water, 200 to 300 pounds.

3. *Portland Cement*: Portland cement is an artificial silicate produced by intimately blending clayey and calcareous materials, burning them to vitrification, and grinding the resultant mass to a fine powder. The following table gives the composition of some well known American Portland cements:

CHEMICAL COMPOSITION OF AMERICAN PORTLAND CEMENTS
PERCENTAGES

No.	Silica	Alumina	Ferris oxide	Calcium oxide	Magnes- ium oxide	Alkalies	Sulphuric Anhydride	Ratio SiO ₂ Al ₂ O ₃
1.	21.22	7.51	3.83	63.75	0.82	not det.	1.58	2.82
2.	21.20	7.90	not det.	63.14	2.40	not det.	1.37	2.68
3.	21.93	5.98	2.35	62.92	1.10	not det.	1.54	3.67
4.	23.36	8.07	4.83	58.93	1.00	0.50	0.85	2.90
5.	22.89	8.00	2.44	63.38	2.30	not det.	not det.	2.86
Ave.	22.12	7.49	3.37	62.42	1.52	0.50	1.34	2.99
For comparison, four well known German cements are given:								
6.	19.35	7.00	4.50	63.75		not det.	not det.	2.76
7.	21.14	6.30	2.50	66.04	1.11	not det.	not det.	3.36
8.	22.69	7.30	2.28	62.28	1.08	not det.	not det.	3.10
9.	24.90	8.00	3.22	59.38	0.38	not det.	not det.	3.11
Ave.	22.02	7.15	3.12	62.86	.86			3.08

As Portland cements have a definite chemical composition, and as the calculation of the chemical composition is a matter requiring a more or less intimate acquaintance with chemistry and chemical re-

actions, no attempt will be made here to set down the method of calculation. For this information the reader is referred to the Geological Survey of Ohio, 4th Series, Bull. No. 3, or to other standard works on cements.

The process of preparation of Portland cement is as follows:

1. Calculation of mixture.
2. Grinding and mixing of materials.
3. Burning of mixture to clinker.
4. Grinding of clinker formed by burning.

For burning the raw mixed material, long horizontal rotary kilns are used. The fuels most used are coal and gas. The clinker formation temperatures vary from 1200 to 1475 degrees C. 1300° C. is probably a good average.

PROPERTIES OF PORTLAND CEMENT

1. HYDRATION

Portland cement stiffens gradually on the addition of water in proper quantities. This hardening is due to the development of crystals. The more the crystal surfaces in contact are developed, the greater the total adherence and the strength of the mass. Crystals in long plates or in interlocked fibres should give greater strength than blunt crystals. This crystallization probably depends upon the amount of water added. About 15 per cent by weight of water is taken to be theoretically correct, and this works out very well in practice.

2. SETTING AND HARDENING

These are two distinct periods. The first is a short period, requiring from 15 minutes to 12 hours, while the second may extend over a number of years. The rapidity of the setting of cement is influenced by a number of factors, which are as follows:

1. Amount of water used.
2. Temperature of water and air.
3. Fineness of cement.
4. Composition of the cement.
5. Time and manner of curing cement.
6. Catalytic agents added to the cement.
7. Composition of the water.

Adding water above the amount required lengthens the period of setting.

Warm water hastens the setting, and, if not too warm, increases the ultimate strength. Boiling water increases the porosity and therefore decreases the strength.

Fine cement sets faster than coarse.

Aluminum and lime cements set quickly, while siliceous cements set slowly.

Fresh cement sets more rapidly than cured. This is due to the slaking of any uncombined lime and to the absorption of CO_2 . Cured cement, when heated, resumes its original rapidity of setting.

Small amounts of certain salts added to Portland cement lengthen the period of setting very decidedly. Thus 67% of barium chloride raised the setting period of a Portland cement from 12 minutes to 580 minutes. A dilute solution of calcium chloride retards the setting, but a concentrated solution hastens it. Soda and potash solutions hasten setting.

Hard water, and sea water, tend to retard the setting.

TENSILE AND CRUSHING STRENGTH

The tensile strength of neat cement increases up to about one year, but it reaches its ultimate strength quite closely in three months. The tensile strength may vary from 600 to 1100 pounds after three months in water. The crushing strength may vary from 7500 to 14,500 pounds per square inch after three months.

Cements are usually tested for tensile strength, because machinery for testing crushing strength is very expensive. Roughly speaking, the crushing strength is from 10 to 12 times the tensile strength.

The following table gives the required tensile strengths in American practice:

Neat Cement:

1 hour in air, 23 hours in water, 100-140 lbs. sq. in.

1 day in air, 6 days in water, 250-500 lbs. sq. in.

1 day in air, 27 days in water, 350-700 lbs. sq. in.

1 day in air, 364 days in water, 450-800 lbs. sq. in.

One part cement (by weight) to three parts standard sand:

1 day in air, 6 days in water, 80-125 pounds sq. in.

1 day in air, 27 days in water, 100-200 pounds sq. in.

1 day in air, 364 days in water, 200-350 pounds sq. in.

The following figures give the breaking loads of Giant cement, with standard sand in the proportion of 1 cement to 2 sand:

Time.	28 days.	3 mos.	6 mos.	9 mos.	12 mos.
Number of breakings.....	690	215	185	155	165
Av. break. wt. lbs. per sq. in.	441	563	657	671	663

The next table shows the influence of varying amounts of water, as found by E. S. Larned:

Brand	% Water used	Initial set. Min.	Final set. Min.	Tensile strength neat cement.			Lbs. sq. in.		
				24 7 28			3 6 12		
				hours	days	days	mos.	mos.	mos.
Giant	15	12	207	371	655	875	941	920	787
Giant	16	29	297	303	750	973	1008	735	816
Giant	18	80	355	260	649	773	831	645	748
Giant	20	143	402	233	500	693	716	621	676
Giant	22	268	473	184	546	635	658	601	589
Giant	24	327	912	167	539	649	644	629	755
Atlas	13	13	270	366	775	859	1067	892	832
Atlas	14	18	303	404	780	891	972	852	781
Atlas	16	22	327	363	602	725	844	806	723
Atlas	18	15	383	308	570	723	785	728	724
Atlas	20	56	703	325	590	718	760	674	636
Atlas	22	52	833	166	554	649	731	643	604
Atlas	24	188	918	42	510	691	695	632	574

THE CEMENT INDUSTRY

For the first time in its history, the Portland cement industry suffered a decrease in 1914. According to the U. S. Geological Survey, the production in 1914 was 88,230,170 barrels, as compared with 92,097,131 barrels in 1913. The shipments of Portland cement were 86,437,956 barrels in 1914, as compared with 88,689,377 barrels in 1913. Stocks of cement at the mills increased from 11,220,328 barrels in 1913 to 12,893,863 barrels in 1914. In May, 1914, mills were operating at 60% capacity, and at only 50% capacity in June.

The Lehigh district of eastern Pennsylvania and western New Jersey is the largest cement producer in the United States, having about 28% of the total production. This district showed a decrease of more than 9% in both production and shipment of Portland cement. The Illinois and Indiana district showed a slight decrease, and the Pacific coast district decreased 12%. Important increases in production and shipment were shown by New York state, the Michigan-Northeastern Indiana district, the Iowa-Missouri district, the Maryland-Virginia-West Virginia district, and the Rocky Mountain district.

The production of natural cement in 1913 was 744,658 barrels, as compared with 821,231 barrels in 1912. The production of puzzolan and Collos cements in 1913 was 107,313 barrels, as compared with 91,864 barrels in 1912.

The value of the production of Portland cement in 1913 was \$92,557,617, as compared with \$67,016,928 in 1912. The figures for 1914 are not available, but will show a decrease. The value of the production of natural cement was \$345,889 in 1913, as compared

with \$367,222 in 1912. The value of puzzolan and Collos cements produced in 1913 was \$97,663, as compared with \$77,363 in 1912.

The imports of all cements in 1913 were approximately 84,630 barrels*, probably 95% of which was Portland cement. The imports show a continuous decline for the six years ending with 1912.

ARIZONA DEPOSITS

Very little information can be obtained regarding deposits of cement materials in Arizona. These materials are known to exist in many places, as at Flagstaff, Phoenix, Tucson, Bisbee, Douglas, in the Tonto Basin and other localities.

So far as is known, there is no plant in Arizona producing any of the three types of cement. In 1905 the Government started and operated a plant at the Roosevelt dam to furnish cement for the construction of the dam. This plant was sold to private parties after the completion of the dam and removed to Phoenix, where it was intended to be operated as a commercial plant.

GEOLOGICAL CONDITIONS

Most of the thick and extensive limestone deposits of the United States are marine deposits, formed by the accumulation on ancient sea bottoms of skeletons of calcareous organisms, such as coral. Many limestone deposits are the result of deposition from solution, but this forms only local deposits.

Clays are derived from the decay of older rocks. Shales are clays which have been hardened by pressure. Slates are a form of shale in which a fine, even and parallel cleavage has been developed by pressure.

Natural materials for puzzolan cement are, of course, of volcanic origin. Natural cement materials are formed by an admixture of clayey material with the limestone during deposition.

PRICES AND ECONOMIC CONSIDERATIONS

The price of cement is apt to be a variable quantity. In 1914 the price varied from \$1.005 to \$0.927 per barrel, for Portland cement. The average price of slag cements in 1913 was 91 cents per barrel, and for natural cements it was 46.4 cents a barrel. There is such an abundance of excellent cement material in the United States that undeveloped deposits have little value.

*A barrel of Portland cement weighs 380 pounds; natural cement, 265 pounds, and puzzolan cement, 330 pounds.

The valuation to be placed on a deposit of cement material requires a careful consideration of many factors. Prominent among these are the demand for and scarcity of limestones; chemical composition of the material; physical character; amount of material available; location of plant, with respect to transportation routes, to fuel supplies, and to markets. Some of the factors have already been discussed earlier in this bulletin.

As to amount of material available—each barrel of Portland cement requires approximately 450 pounds of limestone and 150 pounds of clay or shale. A 1000-barrel per day plant will therefore use, in an ordinary year, about 66,000 tons of limestone and 22,000 tons of shale. Assuming average density for these materials, this same plant would require about 1,000,000 cubic feet of limestone, and 250,000 cubic feet of shale in a year. As the initial cost of a plant is high, allowance should be made for at least 20 years supply under ordinary circumstances. The 1000-barrel plant, therefore, should have 20,000,000 cubic feet of limestone and 5,000,000 cubic feet of clay or shale on its properties.

Cements are bulky, and require cheap transportation. The plant should therefore be close to its market, and should have more than one railroad for transporting its product. It should also be close to a fuel supply, so as to reduce charges on fuel. Fuel cost is about 30 to 40 per cent of the total cost of making cement.

FUTURE OF THE INDUSTRY

The cement industry is in its infancy as yet. Cement is finding an increasing use in every way, in mining, in agricultural work, in road building, in building construction, etc. There seems to be almost no limit to the possibilities for its use.

In Arizona, with the great amount of mining going on, with an assured increase in population, and therefore in construction work, it would seem as though a plant to supply the needs of the various enterprises should surely be successful.