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CHEMICAL CONTROL--INFLUENCE ON MANUFACTURE AND  
QUALITY OF CEMENT.

by  
Joseph Owen Hunt.

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A

THESIS

submitted to the faculty of the  
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI  
in partial fulfillment of the work required for the  
DEGREE OF  
CHEMICAL ENGINEER  
Rolla, Mo.

1931

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Approved by W. T. Schrenck  
Professor of Chemistry.

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## INTRODUCTION

Definition:- Portland cement may be defined as the product obtained by finely pulverizing clinker produced by calcining to incipient fusion an intimate and properly proportioned mixture of argillaceous and calcareous materials with no additions subsequent to calcination excepting water and calcined or uncalcined gypsum.

While a review of Portland cement analysis would show a wide variation in chemical composition, it must not be supposed that such latitude in proportioning the raw material really exists. If the resulting Portland cement is to be sound, normal setting, and of good strength it is imperative that the raw materials shall be correctly proportioned as to the balance between the silica and alumina on the one hand and the lime on the other. Cements from different mills often vary several percent from each other as to the silica, lime, and alumina, and yet one appears to be as good as the other. This variation in composition is due in part to addition of gypsum to, and the contamination by the coal ash of the clinker and also to the absorption of carbon dioxide from the air.

## COMPOSITION OF PORTLAND CEMENT

In order to appreciate fully the need for accurate chemical control in the cement industry it will be necessary to describe the composition of cement. Cement is such a complex substance that two lots having identically the same analysis, fineness, etc., may yet have different setting properties. This difference is due to a difference in the chemical structure in the two cements. But whatever may be the nature of their combination with each other the essential elements of Portland cement are lime, silica, and alumina. The other compounds, while they may exert some influence on the properties of cement, are not themselves of any importance and are merely present as impurities.

Rankin(1) investigated all compounds formed when any mixture of these three oxides is heated at a high temperature and collected the necessary data to plot the relation between the three oxides. His complete diagram is shown in figure 1.

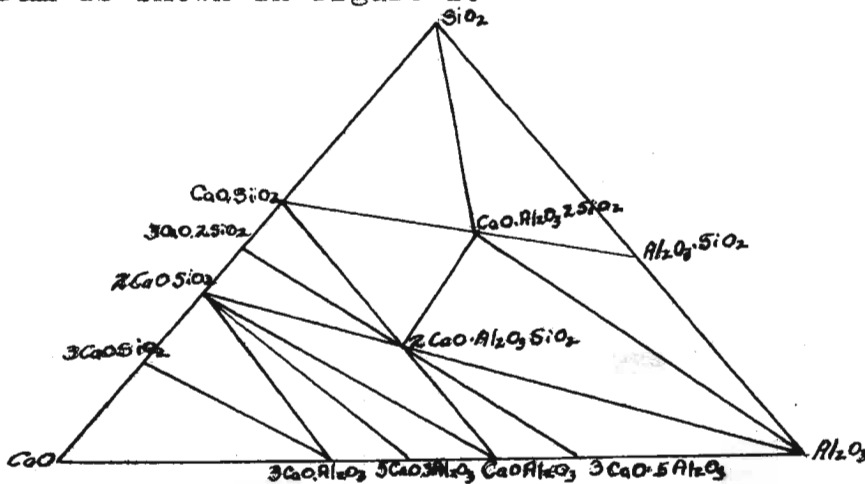


Figure 1. Rankin's Diagram.

Other investigators have shown that only a few compounds are present in cement, however, we are interested only in the small portion of this triangle in which the more basic compounds lie. By referring to Fig. 2 it will be seen that if we join the points on the left side representing  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $2\text{CaO} \cdot \text{SiO}_2$  with with the points on the lower side representing  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $2\text{CaO} \cdot \text{SiO}_2$  with the point  $5\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  by lines we will

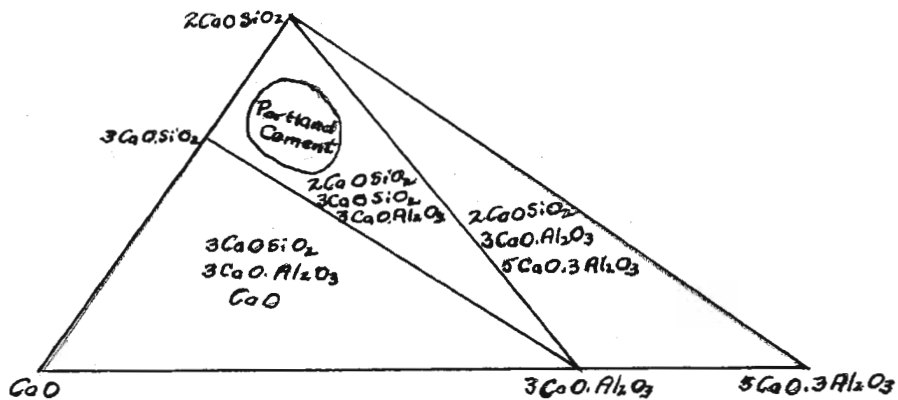


Fig. 2. The region occupied by Portland cement.

form three small triangles. Each of these triangles represent all possible mixtures of these three compounds whose symbols are at the apices of the triangle. Commercial Portland cements will be found to lie wholly within the triangle  $3\text{CaO} \cdot \text{SiO}_2 - 2\text{CaO} \cdot \text{SiO}_2 - 3\text{CaO} \cdot \text{Al}_2\text{O}_3$  and hence are

composed almost entirely of these three compounds. As these cements are not in a state of perfect equilibrium some CaO and  $5\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  are also present in small amounts.

#### RAW MATERIALS

Portland cement may be, and is, manufactured from a variety of raw materials but the essential elements are silica, lime, and alumina. The Hannibal plant of the Universal Atlas Cement Co., gets its calcareous material from limestone and its argillaceous material from shale.

The limestone here contains varying amounts of magnesia, which makes the calculations of mixes more complicated. The percentage of magnesium carbonate varies from 2% to 10%. To be suitable for Portland cement manufacture the limestone should not contain more than 7%  $\text{MgCO}_3$  so the delivery of the stone to the crushers must be carefully supervised to keep the average below this limit. The stone also contains small amounts of silica and iron oxide and the proportion of these constituents must be considered in calculating the proportion of limestone used in a mixture.

Shale, for practical cement making purposes, may be looked upon as merely solidified clay since the chemical composition of the two are very similar and the same regard must be had as to the state of sub-

division of the free silica. Shale is preferable to clay for mixing with limestone since segregation of the two is less likely to take place. To overcome this tendency to segregate, therefore, it is best to mix substances of like physical characteristics.

#### CALCULATION OF RAW MIX.

Many attempts have been made to put the calculations of cement mixtures on a strictly scientific basis and numerous formulas have been proposed for expressing the relation between the lime on the one hand and the silica, iron oxide, and alumina on the other. The order appears to have been reversed inasmuch as the results from physical tests govern the chemical ratios instead of theoretically correct formulas producing high physical tests. After many years of experimenting this company derived a new formula which is known as a molecular ratio. This, as the name implies, is a ratio between the molecules of lime on one hand and the molecules of  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  on the other. It was found that cements made from a raw material with a molecular ratio of 2.75 had the best qualities so this was taken as a standard.



Calculating a shale and limestone mix to secure a desired ratio.

$$\text{formula:- } \frac{\frac{\text{CaCO}_3}{100}}{\frac{\text{SiO}_2}{60} + \frac{\text{Fe}_2\text{O}_3}{160} + \frac{\text{Al}_2\text{O}_3}{102}} = 2.75$$

700 lbs. L-stone  
x lbs. Shale

Analysis

	Shale	Limestone
SiO <sub>2</sub>	57.00	5.00
Fe <sub>2</sub> O <sub>3</sub>	5.00	.40
Al <sub>2</sub> O <sub>3</sub>	19.00	.60
CaCO <sub>3</sub>	2.50	87.00
MgCO <sub>3</sub>	6.00	6.70

Substituting in the formula:

$$\frac{2.5x + (87.00 \times 700)}{(700 \times) 100} = 2.75$$

$$\frac{57.00x}{(700 \times) 60} + \frac{5.00x (.4 \times 700)}{(700 \times) 160} + \frac{19.00x (.6 \times 700)}{(700 \times) 102}$$

By performing the indicated operations it will be found that X=135.8 which is the amount of shale to be used with 700 lbs. of limestone .

The foregoing calculations are correct if the stone is sent to the rock storage as desired but it is impossible to keep the loading so uniform. Consequently other calculations must be made to allow for variable loading in the quarry. Hourly samples are run by acid and alkali for a rapid determination of lime and magnesia. Each scale setting of shale gives a different analytical total so the total clay ( $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ) can be calculated. As the magnesium carbonate is also a variable it must enter into the calculation because when the magnesia increases the lime decreases. A chart was made for varying magnesia at each probable scale setting giving the percent lime necessary for the desired molecular ratio. This is one of the most sensitive methods of control now in use but it turns out a more uniform product than is possible under any other system. The varying magnesia makes the control work here more of a problem than at other mills where the magnesia is constant.

#### CALCULATING THE ANALYSIS OF THE CEMENT CLINKER.

The problem of determining the probable composition of a cement from its raw material is often put up to the chemist. The usual rule is to add together the

percentages of silica, oxide of iron, and alumina, lime, and magnesia and to divide this sum into the percentages of each compound, multiplied by 100, for the percentage of that compound which will be present in the clinker. If this rule is followed, the results obtained for silica and for iron oxide and alumina will be too low and the lime much too high unless oil or natural gas is used for fuel in burning.

In order to determine exactly the contaminating effect of coal ash on the clinker, samples were taken very carefully of the raw material going into the kiln, the clinker coming out and the coal used for burning. Three separate tests were made and the results compared. As a result of this experiment I found that the silica, ferric oxide, and alumina were increased by 0.49%, 0.24% and 0.24% respectively. When the coal burns it leaves its ash in the form of a skeleton, having the same volume as the particles of coal but with only about one tenth of their weight. From the analysis it appears that about one half the ash falls into the clinker. The remainder is carried out by the gas which is estimated to have a velocity of 2,000 feet per minute. In view of this fact the

ash which does contaminate the clinker comes from the impinging of the flame upon the material in the kiln. The ash strikes the clinker and its velocity is stopped by the impact and it either falls among the clinkers or it sticks to the red hot sticky mass. Analysis of clinkers fresh from the kilns shows it to contain about one and one-half percent of pot-ash, soda, sulphur, carbon dioxide, and water combined.

Analysis of raw material

Silica	13.31	
Oxide of iron and alumina	5.18	Mol. Ratio 2.75
Lime	41.13	
Magnesia	<u>2.86</u>	62.48
Correction for ash, etc.,		2.47
Clinker total		64.95
Clinker calculated from corrected total:		
Silica	21.25	
Oxide of iron and alumina	8.72	Mol. Ratio 2.63
Lime	63.33	
Magnesia	4.40	

The contamination by the coal ash changes the ratio from 2.75 in the raw material to a 2.63 in the burned clinker. The addition of gypsum raises

this ratio to 2.65 which is the ratio desired in the finished cement.

#### EFFECTS OF UNBALANCED RAW MATERIAL

The amount of lime a cement may contain is dependent upon both factory conditions and the relative amounts of silica to iron and alumina present. The maximum of lime is usually controlled by the "soundness tests". The minimum of lime is determined by the setting time of the cement, which must be such that the cement does not get its initial set in less than forty five minutes, and also the strength which should be at least two hundred pounds with sand per square inch.

Below are enumerated the effects of raw mixes with an unbalanced lime ratio. (2)

High lime ratio cements have a tendency toward unsoundness, low lime cements being uniformly sound.

High lime ratio cements have good strengths up to ages of three months, but thereafter show little increase and at later ages are inclined towards retrogression.

High lime ratio cements have their setting times retarded while low lime ratio cements have their

setting times accelerated.

High lime ratio cements that are unsound due to their being over-limed, become sound upon being stored for a short time, while high lime ratio cements that are unsound due to underburning require prolonged storage before becoming sound.

Raw mixtures of high lime ratio upon being subjected to extreme fine grinding combine more readily in the kiln.

High lime ratio cements have low specific gravities, the opposite being true of low lime ratio cements.

High lime ratio clinker is of uniformly small size, the other extreme resulting in large irregular clinker.

High lime ratio clinker grinds easily in both preliminary and fine grinding cement mills, yielding large mill outputs and consuming a minimum of power.

High lime ratio cements deteriorate very rapidly on being stored for long periods, the lower lime ratio cements being less affected.

High lime ratio cements have less resistance to all kinds of influences while low lime ratio cements are more resistant.

High lime ratio cements have a tendency towards efflorescence in concrete.

### Effect of Alumina.(3)

Alumina exerts a greater effect on both the quality and manufacture of cement than is realized by some cement mill operators. The relation of the percentage of alumina in a cement to the percentage of silica, namely, the silica/alumina ratio, is of great importance in so far as manufacturing conditions are concerned, and of lesser import in connection with quality.

The relation of the percentage of alumina to the percentage of iron oxide in a cement, namely, the alumina/iron oxide ratio, has a bearing on both manufacture and quality. Cements having exceptionally high alumina contents have correspondingly low silica or iron oxide contents. Such cements have been the most difficult, and in consequence the most expensive cements to manufacture.

As the percentage of alumina (within limits) increases in raw cement mixtures, the temperature required for burning increases in proportion, affecting output and kiln fuel consumptions.

Ring formations in kilns are due in part to high alumina content of the raw mixtures, and in coal fired kilns where coal ash combines with the raw mixtures, this is particularly true.

High alumina clinker is greenish of color and uniformly small in size.

High alumina clinker has a tendency towards unsoundness.

High alumina clinker is exceedingly hard to pulverize in both the preliminary and fine grinding cement mills.

The higher the percentage of alumina present in a cement, the quicker will be its set. Quick setting cements due to alumina are little affected by the increased addition of gypsum. High alumina cements of initially normal setting time, due to decomposition on storage, may become quick setting.

High alumina cements have a tendency towards unsoundness and show the greater expansions. High alumina cements have the higher heat of hydration, and show irregular increase in volume.

High alumina cements, though showing normal strengths at early ages, are inclined towards retrogression at later ages.

#### Effect of silica.

The silica from the shale and limestone in the raw mix is taken care of by the calculations but



this does not allow for the flint which is also present in the stone. Only by the inspection of the rock as it is fed to the crushers can this be detected and an allowance made for it on the hourly calculations. As silica requires more lime for the silica-lime compounds than alumina or iron oxide, a higher lime must be carried to get the desired ratio.

High silica cements are usually slow setting, but of good tensile strength.

High silica cements harden slowly and usually show a progressive gain.

High silica cements are harder to burn in the kiln.

High silica cements are hard to grind both in the preliminary and fine grinding mills.

#### Effect of magnesia.

At one time magnesia was considered dangerous, now the standard specifications allow five percent, and recent investigation places the limit above this. The popular supposition seems to be that magnesia in considerable amounts causes cement in time to expand and crack. Cements in which magnesia replaces lime are of low tensile strength because magnesium com-

pounds have only faint hydraulic properties. Nearly all experimenters agree that magnesia in cement has practically no hydraulic value.

Cement can be readily burned in a rotary kiln with a magnesia content of about 9.5 per cent before the resulting clinker will be materially different from that of a cement containing 3 per cent or less. Very high magnesia clinker is very vitreous and dusts slowly, starting within twenty-four hours.

Cements containing up to 9.5 per cent magnesia show normal set with a slight tendency toward slower final set. With a greater content, there was a quick initial set accompanied by a very marked rise in temperature.

The strength developed either by the neat cement or 1:3 mortars or 1:6 concrete up to a period of half a year, shows that cements containing as much as 7.5 per cent magnesia are satisfactory. Further, the increasing magnesia reduces the rate of hardening so that at the late periods cements with a higher content have rather commendable strengths.

Magnesia lowers the clinkering temperature of

the cement and hence makes a more fusible clinker, and a more easily burned cement. In view of the evidence recently collected, it seems safe to say that magnesia in cement does not cause unsoundness.

Whether magnesia should be considered in calculating cement mixtures is a debated point, as the question is simply whether or not the magnesia is combined with the silica and alumina in cement. If it does combine, enough of the silica and alumina should be present, not only to form the proper lime compounds, but also the proper magnesia compounds, or else the cement will be too basic and will probably contain excess of uncombined lime.

In my calculations for raw mixes I consider magnesia as an adulterant and merely takes the place of so much lime.

#### CORRECTING THE MIX.

On this plant, as on many others, the hourly control samples are taken from the discharge end of the raw material tube mills. If, after the lime and magnesia determinations, the mix is found to be unbalanced nothing can be done about that which has already been ground, but the shale proportion is either raised or lowered to correct the fault. As

the ground raw material is conveyed directly to the tanks over the kilns there is no chance of mixing a high mix with a following low mix to get a balanced composition. Some of the newer plants have installed blending silos to take care of this. The ground raw material is conveyed into concrete tanks and the high and low composition balanced off by withdrawing from two or more tanks at the same time to supply the kilns.

An ideal method for correcting the composition would be to make an approximate mix at the crusher or before the grinding and then use two sets of tanks or bins. One set of at least four or six tanks should be placed after the preliminary mills and one set of four or more after the secondary mills. The tanks should be equipped with automatic samplers so the contents could be sampled as ground. The mixture from the first set of tanks could be corrected to the standard ratio and then after being fully ground could be rechecked and any necessary change made at the second set of tanks.

The starting point in the manufacture of cement of uniform high quality is largely one of absolute control of the chemical composition of the mixture

fed to the kilns. Occasionally a plant is met with where the raw grinding or burning equipment is insufficient, but for the most part the failure to control the chemical composition of the mix is responsible for any irregular quality of the product.

Chemical analysis of the cement does not always show the trouble particularly when this analysis is confined to a sample representing a large quantity of cement, such as a bin of several thousand barrels or a day's run, because such a bin of cement may be the average of several hours of very high-limed and consequently unsound cement mixed with several hours of cement low in lime; the average of the two being often near the desired chemical composition but the physical properties of the resulting cement having something of the undesirable characteristics of both the high-limed and low-limed clinker.

Such a result is quite apt to occur in the dry process where chemical control is generally a matter of examination of a mixture already made rather than of two materials about to be mixed. The routine tests of the dry mill laboratory are usually post mortems rather than diagnoses and are of no value so far as correcting the composition of the particular lot of

raw material under examination is concerned, but serve only as a guide to the making of succeeding lots.

#### COMPOSITION OF COAL FOR CEMENT BURNING.

It may seem to the uninitiated that the chemist's responsibility ends with the delivery of the raw mix to the kilns. But this is not the case as the fuel used in burning must be carefully inspected to secure the maximum fuel value for the least expenditure.

Formerly it was believed that the only coals suitable for burning in the pulverized condition were those high in volatile matter such as bituminous coal and lignite. This supposition was based on the fact that such coals ignite more readily than do the low volatile coals. As a matter of fact, the employment of high volatile coal was influenced largely by the low price at which this fuel could be obtained and the ease with which it could be pulverized.

It is quite probable that the prices being equal, high volatile coal is to be preferred because the rapidity with which it ignites would seem to make fine grinding less necessary; its soft structure also makes pulverizing comparatively easy. The temperature of the flame obtained from powdered coal, however,

is so high, that practically all grades of coal can be burned under suitable conditions. Given a number of coals to select from the question would be one of economy - that is to say, the cost of the coal delivered, the expense of its preparation and its thermal value, rather than its chemical composition.

The coal now most generally employed for burning is gas slack and should fill the specifications below:

Volatile and combustibile matter	30-45%
Fixed carbon	49-60%
Ash	(Not over) 25%

The ash, when under the limit specified, of course merely takes away from the fuel value of the coal. Above this limit it is hard to burn satisfactorily. Sulphur has no effect on the burning, except in large quantities. Iron pyrites are hard, and consequently may not pulverize. When coal containing much of this is used the pyrites may remain in coarse crystals after grinding, which are not blown in the kilns and burned, but fall from the nozzle of the burner among the clinkers and remain unoxidized. When they are ground with the clinker the resulting cement develops brown stains. Practically none of the sulphur enters the cement, except as above.

## MISCELLANEOUS CONTROL WORK.

Besides the task of keeping the quality of the cement up to a high standard the chemist must also assist in keeping operating costs to a minimum. All the firebrick used in kiln linings must be carefully analyzed to select the right brick for the purpose. Due to this practice the relining cost of kilns has now fallen to a very low figure compared to previous years.

A constant check is made on the flue gas from the kilns to insure a proper air supply for burning the fuel. As all kiln men burn by sight they must be checked up on regularly to avoid the waste of fuel and underburning clinker.

The proportion of gypsum added to the clinker is supervised by the laboratory and the  $\text{SO}_3$  content of the finished cement noted. As the A.S.T.M. specifications will not allow more than 2% this control work must be accurate.

All in all the laboratory must be responsible not only for the quality of the product but also for a good share of the actual manufacture. In the cement industry the laboratory really comes into it's own.



## CONCLUSION.

Most non-metallic minerals are prepared for ultimate use without any chemical change in their constituents, or if changed chemically they are not reduced to simple chemical elements of fixed and definite physical and chemical properties. Metallic ores, such as copper ores, are melted and refined to metals of definite purity and with definite properties. Copper is copper wherever or however it is produced. But no two limestones or no two clays or shales are exactly alike and they cannot be made exactly alike.

Different raw materials require different methods of production and preparation. No universal method of proportioning these materials is as yet available and will not be until the scientists discover exactly what happens inside the kilns. The laws which control the reactions are fixed but the reasoning of man is fallible.

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