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William Alonzo McCanless

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PROBLEMS IN THE CEMENT INDUSTRY

by

W. A. McCanless

A

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PROBLEMS IN THE CEMENT INDUSTRY

The major problem of the cement companies is the matter of marketing the product in sufficient quantities and at a price which will return a profit; however, there are some other problems that are of great interest to the engineers, i.e, the interest in the economics of cement based largely on its effect on the cost of contemplated structures.

Up to the present time, I am sorry to say, engineers have done little toward aiding or demanding their rights in the commercial cement manufactured by the cement industry. He is very careful to grade and test his rock and sand in every way possible; he watches his c/w ratio closely but this work is all for concrete, he hasn't thought so much about the cement; in fact, the engineer writes a strict specification on everything in the concrete but the cement. On this he may, or may not, mention the A.S.T.M. specification. If a government or state engineer, he sends a sample to his respective government or state laboratory, or if he is an engineer in private practice, or connected with some structure other than government or state, he sends his sample to a commercial laboratory if he wants a test made.

All these laboratories make these tests in the same manner, for every 200 bbls. of cement a set of briquettes are made, using one (1) to three (3) mortar A.S.T.M. specifications, and broke for tensile strength - in seven (7) and twenty-eight (28) days. The cement is then tested for ignition loss, sulphur setting time, boil fineness,(some laboratories make compression test) and that is all. After they get these accepted tests what have they found out about the cement? Very little, if anything. Quite often these briquettes are not even broken, the pressure added up to the point of A.S.T.M. standards, and the brick taken out and O.K'ed.

The c/w ratio worked up by the Cement Association and A.S.T.M. in itself is a fine thing but of not much use when the test is made with one brand of cement and then another brand used in the actual construction of a project. I mean by this the A.S.T.M. specifications are so low that some manufacturers can do a great deal more than double this test, but the engineers still specify six (6) sacks of cement per yard of concrete, or whatever he considers the cement content should be in a structure. He is still specifying by the sack, regardless of the strength and quality variations in cement. If in making a test a high standard cement is used, and we will say with a c/w ratio of .7, and we obtain a compression test of six thousand (6,000) lbs., this testing being made in a laboratory, when the engineer goes out on the job, he allows the contractor to make his purchase of cement wherever he pleases but the contractor is informed that his sand and rock must be so and so, quite often condemning a gravel and sand pit and barring the material from the job. If this is done there isn't any doubt but that it was necessary but the cement isn't mentioned as long as it passes the

A.S.T.M. and in some cases within the last two years, contractors have been allowed to use cements that do not even come under the A.S.T.M. specifications and are not even a Portland cement.

But we will say that the request has been made and the A.S.T.M. standards have been lived up to. The engineer has known for some time about the c/w ratio and he understands his A.S.T.M. specifications, A.S.T.M. being the one thing he heard a great deal about in school, and since he has been out he hears A.S.T.M. along with c/w ratio, especially c/w ratio and you will quite often hear the remark from an engineer--that there is very little difference in cement as long as it passes A.S.T.M. Well, he is ready to start work on his structure. He is very careful to get his cement water ratio correct and he uses the most accurate method to get his aggregates just right, getting moisture content, etc., but he comes out with a test of 2500 lbs. What is wrong?

I will venture to say that more than 95% of the engineers will dismiss the thought from their mind with the idea that the gravel and sand has fallen down, but this is not true. The brand of cement he has used cannot go over the strength he has obtained in the field, while in his laboratory tests another brand was used and he obtained a strength of 6000 lbs. with the same c/w ratio. This is very misleading to the young engineer, and ofttimes to the practicing engineer with a great deal of experience behind him, due to the fact that they have not been educated in cement, all their education being in the finished product, i.e. concrete.

The aim, then, of every cement manufacturer is to manufacture a product of maximum quality at a minimum cost. The cost is usually laid down by the management of the company based on market conditions and the manufacturing organization must operate for a quality consistent with the figure.

A brief outline of the trend of the industry may be of help in developing the problem, as well as explaining some of the solutions that have been made. The rotary kiln is the most recent revolutionary invention pertinent to the manufacture of Portland cement. Our inventions have been made from time to time and improvements have been in operation but for the most part they have been in the strictest sense developments rather than revolutionary inventions. The same may be said of the uses of cement. The only invention I think of at this time which has materially affected the use of cement has been the automobile. The progress in the use of cement then has been largely one of development and increased spread in the use of previously established types of construction. The advancement of the equipment and processes of manufacture has been largely developed by the chemical or plant engineer. The rotary kiln has grown from some 60 feet in length to 400 ft. The dismeters have been enlarged to the extent that production has been increased some ten times that of the 60 foot kiln. Grinding machinery has been improved to about the same extent. The result is a very marked effect on the operation of cement plants on account of the difference in production per unit of machinery.

The machine development has been largely accomplished by the manufacturers of cement making machinery with some slight borrowing of machinery developed for use in other lines of industry. A target of quality has been maintained by the A.S.T.M. for the machinery manufacturers to meet and they have for the most part developed production units which will operate with economy and yield products exceeding the specifications. In many cases they have gone further and improved some details of the quality of the cement. In essentially every case, however, the aim of the new equipment has been for an increase in strength or for an effect on the operation cost of some other unit in the plant. It is further noteworthy that these developments have been made more or less piecemeal and every piece of equipment has been made to fit in with the normal flow of the old established order of cement plants. The capital investment involved in the large production units is heavy but would be entirely prohibitive if each unit introduced called for scrapping of the entire plant.

In spite of the fact that the units do not demand the scrapping of the entire plant, the cost has been heavy and most managements have felt that they were doing their bit in keeping up with the times with the purchase and operation of the newly development equipment. Research suffered in the cement manufacturing organizations on this account.

Up to, say ten years ago, a chemist was doing his duty by his organization if he manufactured a cement with 10 to 20 per cent factor of safety in the matter of the A.S.T.M. specifications.

Plasticity was considered to some extent and some manufacturers even went so far as to manufacture special products of this nature. At this time a number of plants had been operating for some time with large production units. Many of these plants were showing an increase in strength of their product with respect to the cost, while others preferred to take the entire profit for their own books, until it was suddenly discovered that cement plants had been built considerably in excess, from a production standpoint, of the normal consumption of cement.

In other words, a buyer's market had been created and the idea started to grow that it was not only necessary to meet the specifications but it was further necessary to create interest to maintain sales. As we were still measuring the quality of the cement on a strength basis, the first move was to attempt to increase the strength for the production of a product that would be outstanding, either from the high strength obtainable or the economy from a cement factor standpoint of the concrete. We could see that the engineer while favoring concrete construction disapproved of the long curing period required. Finally, as a development, the High-Early Strength Cements appeared. Fine grinding and somewhat harder burning was the basis used for the manufacture of most of the cements of this type. The problems introduced by the former were mechanical, while the latter was one largely concerning refractories. Composition tended to higher lime values but little was actually known at the start. Later the

High Early Strenth Cements were criticized on account of excessive heat of setting and hardening and we began to have a new school of thought developing in the matter of quality.

This brings us to one of our present greatest problems--namely, a suitable standard of quality, or qualities, for cement. The investigation which the University of California is now completing is looked to by operating cement chemists and engineers with considerable hope in the matter of at least one type of cement. These specifications for the Hoover Dam give us, to a large extent, a basis of valuing quality and will minimize doubts as to the requirements of a satisfactory quality. Since the old specifications have been somewhat discredited, operating cement men have wondered what would be wanted and, to some extent, have tried to influence the wants.

The University of California investigation is free from many problems of a research organization connected with a manufacturing institution. Their equipment is small and flexible. Changes can be made with minimum difficulty and with no operating plant or set of equipment in mind. Materials may be obtained at will and compositions altered to suit the studies in mind. The operating chemist or the research engineer connected with an operating organization must show a profit to his organization to be permitted to continue his activities. He must, therefor, largely restrict his work to a nature which will fit with his available equipment and raw materials or at least fit them with changes involving only minor capital investments.

To illustrate the workings of the generalities so far outlined, I should like to trace the line of thought in connection with our problems at Merced, merely to permit them to be a little more specific:

During our period of construction it was realized that in order to sell cement in the territory we could reach with a reasonable freight haul we would have to do something to create interest in the cement. An advertizing campaign might accomplish this result but its cost with respect to the profits per unit weight would likely prove prohibitive. For this reason it was decided the best results could be obtained if the interest could be created by the product itself. Outstanding performance was of course necessary. The plant was designed at that time and under construction. Large and efficient production units were being put in so that from a mechanical standpoint it was believed that we would have as modern equipment as was available on the market. The matter of limestone was fairly well determined by the property owned by the company. This rock was of the so-called rock nature carrying quite high contents of silica with respect to the iron and alumina. A clay of a sort was available near the plant.

A survey was made of the cements on the local market and to some extent the markets of the United Stages with the view of determining at least the popular compositions if not the best. We found as a result that most of the plants had much more alumina than we would have if only the material from the quarry was used and somewhat more than if the clay near the plant was used. Further investigation disclosed the fact that the clay near the plant was sandy and would require considerable grinding to prepare it for mixing and burning. It was further noted that the amount of clay necessary to mix with our average limestone would be low. In view of these facts we decided on the policy of a high alumina cement. Inasmuch as a high alumina cement required the importation of materials it was decided that as fine a material as possible should be obtained to reduce the strain on the raw mills. The plant layout had sufficient grinding capacity for, we believed, about 92% passing the 200 mesh screen. It was known that finer grinding was beneficial to the reactions in the kiln and believed that wet grinding was better than dry.

Both operating chemists had been accutomed to an operation previous to that time where the limit of the raw grinding mills, with respect to the capacity of the kilns, was about 85% passing 200 mesh. So it was expected the additional fineness of raw material, together with the wet grinding and mixing, would give us a good boost in strength but were a little doubtful of getting as good results as we desired on the basis of some experience with larger units and wet grinding. A calloidal clay was finally adopted of which some 94% will pass a 200 mesh screen. This additional fineness of raw materials we hoped would give enough outstanding strength to at least create interest, especially as the kilns were 240 feet long, providing good burning conditions, and the finish grinding mills were of ample capacity to assure cement of a fineness at least equal to standard practice and considerably higher than most operations.

The cement was somewhat outstanding in performance but was disappointing as it was felt that the company was not getting its money's worth in comparison to the small kiln and small grinding unit production. Some economies were made in the matter of labor which compensated for capital investment but that did not concern us so much as the fact that we had to revise our ideas concerning the importance of raw mill grinding, and to some extent, general operation.

Finer grinding than was practiced at that time might be accomplished by some means but due to the small increase that could be attributed to that phase of the process, we were inclined to pass to some other part of the process for the answer. Finish grinding got its chance; but here was developed a limit in the form of fast sets, gelling, and hot grinding mills.

Composition came in for attention next: When the kilns were first put into operation it was realized the composition might not coat very well. Therefore, to protect a high priced refractory lining, it was decided to add iron to the raw material to aid in coating the brick. Some 6000 barrels of cement were made using this composition. The iron content, as Fe_2O_3 in clinker, was about 6%. Eventually this clinker was ground to cement along with the high aluminous cement without the addition of iron. Finally, we observed that both products gave good early strengths while the clinker with the iron seemed to be better at the longer time periods. The high alumina cement gave troubles enough to make us want to avoid its use. The cement gelled, was inclined to want to set fast and did not store well. Work on heat of hydration was not thought of at that time but there had been sufficient evidence to decide to keep the alumina to a minimum value. We therefore organized with the quarry to supply a lower lime valued rock so that a minimum of clay was necessary. The iron addition, we knew, would be too costly for our purposes at that time. The new composition was radically different from that previously used as the silica content was raised from 21 to 24 or 25%; the alumina was reduced from 6 or 7 to 3½ or 4%; the iron content was raised only slightly and the lime content was raised somewhat; the magnesia content remained the same. At this time information was available on the structure of the compounds formed by burning clinker but it was considered mostly in the light of the potential compound; in other words, it was assumed that a given set of oxides would burn to a given set of compounds and that the only important phase was the removal of the free lime and the insoluble material.

An investigation of some of the allied industries, smelting, glass manufacture, and ceramics indicated the importance of conditions on the resulting compounds forming and gave us a rather different picture of the conditions we were facing in the matter of composition. Properties of glass, we found, were much more dependent on the way it was heated, the temperatures attained, and the time submitted to each temperature. Properties of slags were likewise very decidedly affected by time and temperature conditions set up in the kiln. We reasoned that if the properties of these products were materially affected by time and temperature and that they contained about the same oxides as the cement manufacturers must use, they must follow the same course. If an improvement in the product was desired it might be well to affect the structure of the clinker from a physical standpoint, either by changing the crystalography or the chemical composition and still maintain essentially the same oxide composition.

A basis for a line of reasoning to lead to satisfactory conclusions was reached with difficulty, but finally a conception, new to us at least, of the reactions taking place in the kiln gave us a start. It had previously been believed that the order of reaction in our wet kiln was, first, a period or zone of drying the slurry, then a zone of calcining the limestone to lime, followed by a period of absorbing heat and finally a melting of acid constituents of the mix which would absorb the quick lime previously formed and produce the clinker that was desired. The hotter it could be burned, the better, it was believed. We thought that the nearer we could approach liquid phase, the more complete reaction we would have and the more potential strength to be gotten out of the clinker when it was made into concrete.

Several contributing factors upset this theory for us. Some experiments conducted during the construction period of the plant gave results which were at that time unexplainable and some analytical data previously determined from samples taken from a kiln which was shut down and allowed to cool during the operation, gave food for thought. In addition, references were found showing that the reaction of lime and silica would take place at a temperature of 800° C. This latter fact, coupled with the knowledge that ignition loss was present almost to the discharge of the kiln, upset the idea of reaction zones.

The experiments conducted during this time were performed in an upright kiln, using bars made from the raw materials we expected to employ later. The materials were ground in a small ball mill to 94% passing the 200 mesh screen and then made into bars about 10 inches long and 1½ inches square. These bars were burned in the kiln with some success but a large portion of the clinker thus formed disintegrated. The disintegration we dismissed at the time and ascribed it to lining reaction. The clinker that did not disintegrate was apparently okeh but inmany cases did not boil. We still attributed the difficulty to lining reaction. Finally one burn was made and the test finished late in the afternoon. The kiln was too hot to unload for some time so an iron plate was put over the stack to prevent contamination from dirt and the kiln left till the next morning. On unloading the clinker it was found to be of a brown nature and when ground formed a highly satisfactory cement. The results were attributed to a long and soaking heat. An unsuccessful attempt was made to confirm them, using commercial cement for the raw material and reburning. Sacks of several available commercial cements were obtained and mixed with water and made into bars similar to those previously used. The burning was accomplished in graphite crucibles. At first some difficulty with lining was observed but later the crucibles took on coating and that difficulty was removed. We still had trouble with the boil except in an odd case or two where the clinker was allowed to remain overnight. The significance of the result at that time did not register. We considered the result a freak of some sort and blamed the unsoundness onto the hydration reaction in making the bars. We believed that some reaction took place which put the cement into a state that made recombination to clinker difficult. We knew at the time that work on reburning clinker was being practiced with some degree of success but that they used fresh clinker and temporarily dismissed the unsoundness.

Several other disconcerting facts presented themselves about this time. First, the higher limed compositions ground to satisfactory strengths more readily than the lower limed products. Visual inspection of the clinker and behavior in the hot zone of the kiln indicated that the high lime material was not as near to the slag point as the lower limed materials. It was further noted that the clinkers made with the minimum of clay ground to satisfactory strenghts more readily than those containing a large amount of clay for the same lime content. The better products appeared, in the kiln, to have less evidence of liquid phase than the more unsatisfactory products.

Finally, the startling results of the brown clinkers were remembered and several rather disconnected tests were made to try and reproduce the brown materials.

The oxide analysis of the brown material was known to be the same as the black clinker. The brown material tended to be more friable. The difference, we then assumed, must be of a structural nature with a possibility of some of the iron being affected. Hot clinker was quenched with water, the clinkers subsequently dried and ground to cement. Some good results were obtained but more unsatisfactory results were obtained than good ones until it was found that the quenching must take place at high temperatures and the drying must be controlled to keep the clinker at a very low temperature.

These results finally started us on a lime of thought that has since become the basic principle of our operation. The old schools of physical chemists taught that some reactions were reversible and others were not. The newer schools teach that all reactions are reversible, from a theoretical standpoint, at least. The direction of reaction then becomes not a matter of material present but a matter of the conditions to which these materials are subjected. Clinker, we found, was not the stable material we had once believed it to be but an unstable compound, or group of compounds, quite sensitive to temperature and possibly some other outside conditions. Our conclusion was that we must not consider burning cement as a matter of getting the materials up to a given temperature and forgetting about it, but the entire heat system must be taken into account from introducing into the kiln to the time the clinker is cooled to approximately normal temperatures.

To make the matter a little clearer, let us assume for argument that a set of conditions could be set up by which the raw materials could be burned to a clinker and finally reverted back to their original state. Clays in nature are formed from oxides which have previously been combined by heat reactions from volcanoes and the reversibility of the reaction between CaO and CO_2 is too well known for further comment. We will then set up as our problem for solution in the matter of producing clinker, not merely the heating side of the reaction, but also the cooling side of the reaction.

Several questions are up for answer at this time. For the most part they have to do with the properties of a desirable clinker. Is it necessary for all of the material to be crystalline and of definite molecular composition? If not crystalline, to what extent should the congealed melts be present? If these questions could be definitely answered the problem would be rather simple in solution as the laws of crystallization are fairly well established.

Heating to proper temperatures will cause melting in eutectic proportions, easily determinable, and controlled cooling may be employed to produce predetermined proportions of crystal with respect to congealed melt or glass. The glass and ceramic industries both depend on such processes. Our problem, however, is not quite so simple. First, we have no satisfactory way of separating the crystals from the melt for analytical purposes or for testing; second, clinker is not our ultimate aim but merely an intermediate step in the process of cement manufacture.

Our scheme of working on the problem has set as an end point the cement in concrete. We have set up two standard mixes. They are made from aggregates screened to clear gradings and then recombined in definite proportions to make a repeatable concrete mix. One mix employs a cement factor of five sacks per yard and the other six sacks per yard. The water cement ratios are 1.00 and .8 respectively by volume. The compressive strength of 6 x 12 cylinders is used as the final analysis of the quality of the clinker produced. Smaller specimens are used to some extent for indicative results. From this point we work backwards in the manufacture of cement to the desired point of operation for investigation.

Three types of grinding mills have been employed in the tests. A small mill some 12 inches in diameter and 18 inches long is used for small scale tests. Most of our laboratory grinding is done with a mill 24 inches in internal diameter and 30 inches long.

This mill for some purposes is loaded with varying grinding media and run various grinding periods but for the most part is operated on a standard grinding condition of 2000 revolutions at the rate of 33 r.p.m. The third mill is a 7 x 26 foot compeb mill of commercial operation. The larger laboratory mill operated on normal clinker gives a reference to the operation we may expect for commercial operation. Grinding for the period and rate mentioned with a charge of 750 pounds of 7/8" balls, a clinker charge of 150 pounds, together with a gypsum addition for a suitable sulphur trioxide content gives a strength performance well within experimental error at the large mill operated on commercial rate with commercial clinker. Increases in strength determined in the test mill may be checked out in the commercial mill and may be used in either of two ways. The increase in strength of the product may be obtained with the normal grinding rate, or a product of strength equal to the previous normal may be obtained at a more rapid rate to show a manufacturing profit. Several hundred laboratory tests have been checked against a large number of commercial tests to confirm the accuracy of the scheme as a testing medium. With a testing medium at hand we were then able to go ahead with the clinker. The first steps were in the nature of elimination contests. The kiln was first considerd. It was assumed that the cooling condition of the normal rotary cooler would be constant and changes in kiln operation could be effected and cooled in the standard way for study. The old idea of soaking heat led to the belief that a longer burning zone would help. We realize that hopes along this line were rather remote as in normal operations we have three types of fuel, which, in themsleves, make for different lengths of burning zone. Gas burns with a short flame close to the discharge of the kiln; fuel oil, due to its physical state, atomizes more slowly and makes a longer flame and powdered coal has a still slower rate of combustion and makes for still longer flame.

In view of the fact that other conditions were variable, some hope was held for a longer flame. A burner for this purpose was designed and installed in the kiln. In addition, the feed end of the kiln was throttled down for better draft control and finally a ring was installed in the discharge end of the kiln to retain the clinker in the kiln for a longer time.

The long burning zone and draft control paid from an economical standpoint, as fuel consumption was somewhat lowered and refractories for lining burned out more uniformly, but from a quality standpoint little change was made.

In a cement operation cooling starts before the material is discharged from the kiln. The fuel is admitted through a small orifice and spreads to the diameter of the kiln. During this spread the pressure of fuel and primary air introduced, together with the draft of the kiln, draws the flame back some considerable distance from the discharge. As a result a so-called nose ring is formed at or about the lower end of the hottest part of the kiln and the distance from the nose ring to the discharge of the kiln is a cooling zone. The position of the nose ring in the kiln is a function of the type of fuel used and the conditions under which it is used. The slower burning of the fuel, the farther back in the kiln do we find the nose ring.

As previously noted, the glass maker depends on cooling rate to prevent crystalization. He heats his materials until they are melted, then cools rapidly to prevent crystalization. If his material is kept in the plastic state for too long a period of time, crystallization will start and the glass will devitrify. Their practice is to cool rapidly, which prevents crystallization, but at the same time sets up internal strains which are eventually relieved by annealing. Common glass melts at about 1100° C; it is cooled rapidly and then annealed and the glass formed into the desired shapes below 800° C.

At the time we were making the tests on the kiln we believed that we wanted crystals and not glass in the clinker so we decided that the thing to do was to make the cooling rate slow for the start of the reaction and give the crystals time to form. That was the reason for the discharge baffle. We believed that the clinker leaving the burning zone would be subjected to some heat from the flame even though it had passed the most intense portion, and further, that the larger mass of clinker would cool slower due to specific heat. The reasoning was good but the results in error. The restriction of the opening at the discharge of the kiln caused a greater speed of the incoming secondary air and the flame was simply carried back farther into the kiln and the distance from the nose ring to the discharge was somewhat greater but the discharge temperature of the clinker was no higher than before.

We then decided to go through the cooling range of clinker. Tri-calcium Silicate was assumed by most investigators to be the most powerful strength producer and, according to Findlay in his work on the phase rule, this compound is formed only on the cooling side of the heat system. He maintains that in the binary system of lime and silica, when temperature is above 1900° C, di-calcium silicate and free lime will exist in the presence of each other, but that as the temperature is decreased below 1900° C, the lime goes into combination with the di-calcium silicate to form the Tri-calcium Silicate. If this is true in the case of the binary system, we assume that it is likely also true in our complex four or five component system, and that if we wish to get large amounts of tricalcium silicate in the resultant cement we will have to control the cooling to give time for the completion of the reaction and also to prevent reversion to some undesirable compound which would impair the quality of the resultant clinker.

A method of determining the tricalcium silicate present was not available and, so far as we know now, authorities are not agreed on a satisfactory determination. Free lime is assumed to be indicative so we used that determination and depended on strength for the rest. If the strengths were good we gave tricalcium silicate in proper form the credit and if not, we tried to account for the result in some other way.

The range of tests made constituted taking clinker from as far back in the kiln as feasible in order to get it as hot as possible and cooling rapidly with air or water, and finally going to the other extreme of cooling the clinker slowly. The slow cooling was accomplished in an insulated iron box. A large iron box, 3 feet cube, was partly filled with clinker. A smaller iron box was then put inside the larger and surrounded with hot clinker. The inner box was filled with hot clinker and covered with an iron lid and then covered with more hot clinker. All of these tests were conducted in parallel with the samples from the rotary cooler taken concurrently. The slowly cooled material outperformed the rapidly cooled. Our direction was established.

The next move was to try for slower cooling still. Insulation at the higher temperatures was not to be seriously considered. We therefore undertook to cool slower by incorporating fuels with the clinker and here we began to get worth while results. Along with the worth while results, however, our problems increased. A possibility of an outstanding product was in evidence but its application was a source requiring lots of work and analysis.

We soon found that the process was not fool proof. On numerous occasions the clinkers prepared under this scheme of cooling in the presence of a fuel were actually toughened to the extent that much lower strengths were obtained. Continued observation convinced us that the higher the temperature we could start the cooling, the better the results would be. This was accomplished by operating the kiln in a different manner to discharge the clinkers at a more rapid rate and thus bring the hot material from the burning zone of the kiln to the condition of treatment quicker.

Later we found that the reducing condition was of more importance than the rate of cooling, or perhaps made the rate of cooling less essential. Clinkers could be quite rapidly cooled in the presence of a reducing agent providing the temperature of starting the reaction was high enough.

Several experimental devices were adopted to affect the cooling rate of the clinker and also to provide for a reducing condition for cooling the clinker. The one outstanding feature of the tests was a demonstration of the fact that the starting temperature had to be high for successful results. The storage time was quite important if no reducing agent was used but, with an incorporation of fuel, could be cut down to a minimum of thirty minutes to one hour. On the basis of such results it was believed that our commercial clinker cooler could be converted into a device for treating clinker.

A stack was provided at the discharge end of the treater and the feed hood was rebuilt to provide for a burner for reheating and introduction of the reducing agent and the entire cylinder lined with fire brick.

With this setup we could practice our scheme in several ways. The clinker could be reheated with a short snappy fire close to the feed end of the treater and then as it passed down through the rotating cylinder it underwent a cooling process in the presence of the effluent gases. In this case the flame was controlled for a minimum of oxygen in the effluent gases. A second variation consisted in operating the kiln in a manner to discharge clinker as hot as possible, then introducing it into the treater and subjecting it to a decidedly reducing flame. Little reheating was effected in this case; the entire process depended on controlled cooling. In the third case a combination of reheating and reducing was practiced with a hot snappy fire for the reheating and the addition of solid fuels (coal and coke) for the reduction.

All of the schemes were successful when practiced under certain conditions of temperature with respect to oxide or potential composition. We did find, however, that different compositions required different treatment. We have been successful in determing a treatment for the range of compositions likely to be manufactured at our plant which will give an increase of some 30% in grindability from a strength standpoint. This, in itself, will make the process commercially worth while. From an investigator's standpoint, we still have a long way to go. We have not determined the limit of the process. We believe that the grindability, with proper treatment, can be effected much more than we have been able to do so far.

Our program for the immediate future has not been definitely charted as results of commercial tests runs are still incomplete. When they are completed we know that there will be many pertinent questions to answer and many problems to solve. We rather expect to follow two general lines. We wish to assemble some data on the structure of the clinker. If possible, we wish to know whether we are making a more or less cyrstalline product. We wish to determine the points of combination and recombination on the cooling side of the reaction with respect to temperature.

Current literature on clinkers is rather confusing. The Bureau of Standards and the Cement Association, together with some other research organizations, propound the theory, with supporting evidence, that normal burning to essentially no free lime gives a group of rather definite compounds. If this is true, then our process is likely one of maintaining the liquid phase for a longer period and permitting the compounds to form larger crystals. Reduction of iron, provided it is not carried too far, lowers the melting point and is inclined to speed combinations of oxides such as we have in cement.

On the other hand, we have reports of other investigators in the literature who admit the possibility of the compounds usually considered in cement clinker but believe that they are only party formed on account of the cooling rate and that the remainder are in the clinker in the form of a super-cooled liquid or glass. If this is true, then likely our process is one of annealing or devitrification. Mr. Dahl, of California Portland Cement Company, and Mr. Colony, of Columbia University, have presented considerable evidence in favor of this theory.

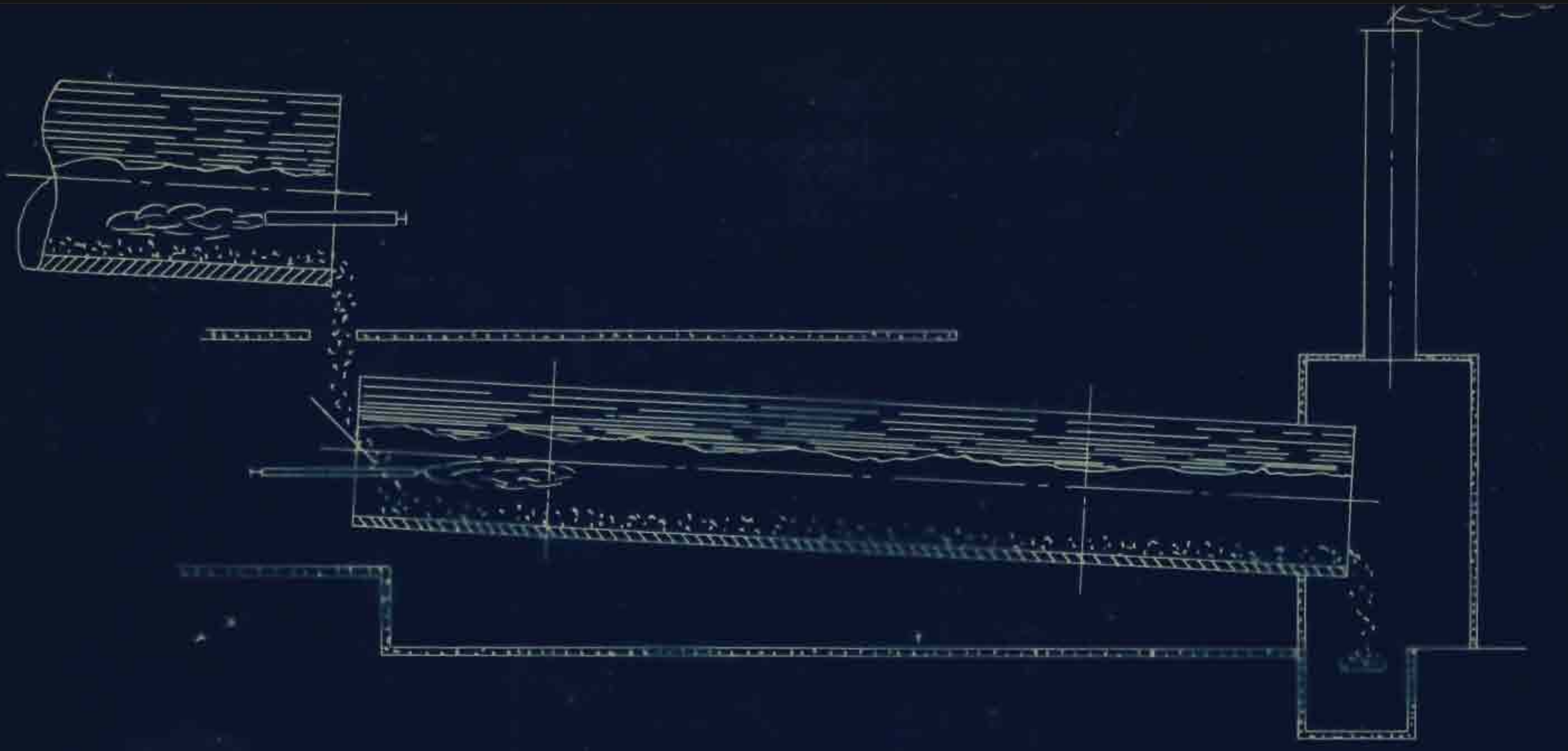
We, therefore, now have as a primary problem, the decision as to which theory to use as a basis for reasoning. We shall likely have to work from both for a time and select the one giving best practical results regardless of accuracy but nevertheless we have been able to reach strength that a few years ago was unthought of.

The City of San Francisco has had some problems on their Hetch Hetchy water project in their tunnel work that are probably different and handled differently than in any other part of the world. While excavating this tunnel they ran into some ground that seemed to creep as soon as it was exposed to the air. However, I don't believe it has ever been definitely decided whether or not the air caused this moment. At any rate, this ground would continue to creep, crushing all the timber and making it necessary to not only remove and replace the timber, but excavate again. It was thought if this ground could be sealed with a material that would reach a strength of 2000 lbs. within a few hours after placing, this slipping might be stopped.

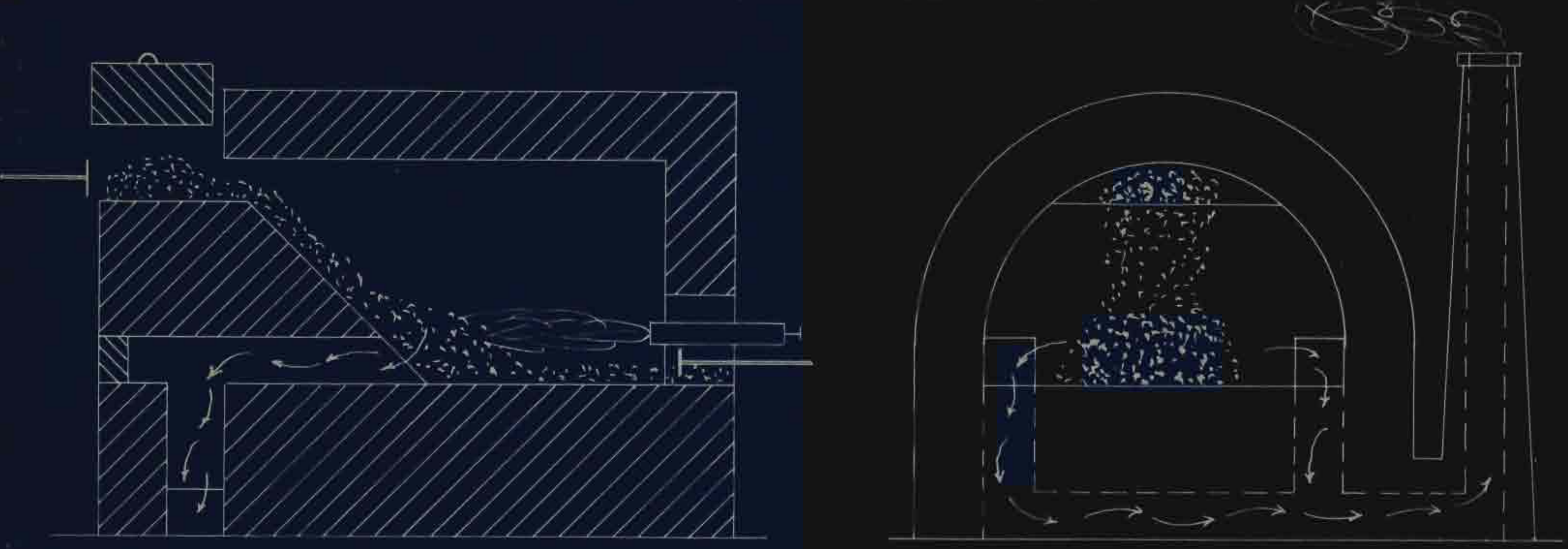
The ground is now being supported by the use of Gunite mortar, made with one part Yosemite "Oneday" cement and three parts sand. (Specifications for this mix will be found on page with strength test curves.) This Gunite is placed fouteen inches thick on the circular walls of the tunnel and within two to three inches of the face of the heading. After placing this Gunite they are able to blast for their continuous work in three hours time, regardless of the fact, as mentioned above, the face of the heading is only approximately two inches from the finished Gunite work.

In building the Golden Gate Bridge, San Francisco, construction of which has just started, it was necessary to move a sea wall out into the ocean several feet. It was first thought and designed that a protecting wall would necessarily have to be constructed in order to protect the new wall during its construction. A portion of this wall was built between tides using Yosemite "Oneday" cement as an experiment. This experiment proved a success, eliminating the necessity of the building of a protective wall that would have cost several thousand dollars. This sea wall is of stone masonry, the mortar mix being a one to three with a small amount of calcium chloride and as small a quantity of water as possible for a workable mix.

In the trial test the mortar had approximately two hours setting time before the waves started pounding on it. The waves were of such tremendous strength and magnitude that they left rock on top of the wall of a size one man could hardly lift, but the mortar held perfectly and the construction of this wall is in progress at the present time.



Yosemite Portland Cement Corp.
Commercial Clinker Treater



Continuous Furnace for Heat Treatment.

Chemical Detail
Paper No. 6

Oxides	I	II	III	IV	V
Silica	21.40	21.94	22.80	22.41	23.02
Iron	1.94	2.05	1.91	1.89	2.39
Alumina	3.40	3.87	4.63	4.71	4.55
Lime	67.60	65.57	65.25	65.36	64.83
Magnesia	1.51	1.42	1.46	1.52	1.62
Sulfur	1.90	1.92	2.02	2.06	2.03
Loss	1.68	2.03	1.06	1.64	1.45
Insoluble	0.23	0.34	0.33	0.17	0.19
Uncombined Lime	1.3	0.50	0.50	0.50	0.50
Compound Composition					
C_4AF	5.90	6.23	5.81	5.74	7.26
C_3A	5.72	6.78	9.04	9.27	8.00
C_3S	77.77	66.13	53.07	54.26	48.31
C_2S	2.09	12.11	24.45	22.99	29.11
$CaSO_4$	3.23	3.26	3.43	3.50	3.45
Kiln Disch. Temp.	2360	2300	2250	2450	2500
Treater Temp.	1600	2100	2350	2400	2300
	2400	1700	1900	1900	

Physical Detail
Paper No. 6

2000 Rev. Grinds

Clinker	Treater Temp.	200 M.	Consistency	Setting time		Tensile			Compression 1-3 Ottawa Sands			
				Initial	Final	1-Day	3-Day	7-Day	1-Day	3-Day	7-Day	28-Da
I	1600	96.0	23	2:10	3:25	200	325	415	1400	3380	3947	5937
	1800	96.0	24	1:50	3:00	195	295	350	1390	3580	4040	6190
	2200	95.0	23	2:00	3:25	210	310	360	1910	3380	4966	6303
	2400	95.5	24½	2:40	4:10	255	370	410	2228	4393	5550	7449
II	1700	92.5	23½	2:05	3:40	165	275	345	1464	2800	4000	5476
	2100	95.5	24½	2:40	4:10	210	310	360	1788	3629	4902	6494
III	1900	95.0	24	2:30	4:10	210	355	410	1783	3310	4329	5857
	2100	96.0	26	2:25	4:20	250	400	430	1719	3510	4456	5602
	2300	95.5	24½	2:05	3:45	205	315	360	1527	3438	4870	6064
IV	1900	94.0	24	2:25	4:05	205	300	425	1719	3438	4650	5539
	2200	95.0	25	2:30	4:10	200	310	405	1592	3640	4657	5937
	2300	95.0	25	2:40	4:15	195	300	375	1416	3100	4520	5746
	2400	92.5	23	2:45	4:20	180	285	350	1220	2810	3700	5093
V	2300	94.5	24½	2:20	3:10	195	270	320	1400	3060	3756	5640
4000 Rev. Grinds												
I	2200	96.5	23½	2:25	3:35	300	350	520	2535	4677	5666	7019
II	2100	96.0	25.0	2:10	3:30	290	375	475	2674	4750	5666	7179
III	2300	94.5	26.0	2:00	3:05	270	430	455	2740	4800	5984	6812
8000 Rev. Grinds												
I	2200	97.0	24.0	1:55	2:40	375	455	515	2992	5491	5730	7321
II	2100	94.5	24½	2:20	3:10	325	420	485	3280	5911	5857	7740
III	2300	96.5	25.0	1:30	2:10	345	425	470	3320	5120	5921	8101

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Physical Detail
Paper No. 6

Cement Composition No.	Grinding Rate	Fineness				Set		Consistency	Tensile				Compression-1-3 Ottawa San			
	Bbls. per Hour	-10μ	-20μ	325M	200M	Initial	Final		1-Day	3-Day	7-Day	28-Day	1-Day	3-Day	7-Day	28-Day
1931 Ave.	52	23	44	80.0	93.9	2:40	4:30	24	178	303	384		1152	2663	3882	
I	30	38	62	90.0	94.4	1:20	2:15	24	285	425	470		2419	4584	6190	
	40	42	64	95.0	97.5	1:30	3:25	24½	260	375	450		2193	4010	5850	
	45	38	66	92.4	96.5	1:15	2:05	24½	255	400	450		2037	3820	5666	
	50	34	58	94.8	97.5	2:35	4:45	25	240	375	460		1838	3963	4919	
	65	32	58	89.0	95.5	2:20	3:30	24½	175	325	400		1620	3510	4585	
II	30	38	60	91.0	91.9	1:10	2:20	24	280	410	495		2355	4322	5838	
	50	33	55	95.2	97.5	1:15	2:05	25	260	405	440		1783	4074	5347	
	65	32	51	83.0	91.6	2:00	3:40	24	165	355	400		1289	3370	4084	
III	44	39	56	93.0	97.5	2:15	3:45	25	270	400	410		1783	3947	4918	
	71	34	51	87.0	94.4	2:30	4:05	24½	185	340	390		1273	3183	3820	
IV	60	34	55	89.2	82.0	1:45	3:50	23½	160	245	290		939	1592	1909	
	65	31	55	88.7	80.5	2:30	4:25	24	130	225	260		885	1273	1592	
						Averages										
I·II·III	30	38	61	90.5	92.2	1:17	2:10	24¾	283	417	483		2387	4453	6014	
	40-50	37	59.8	94.1	97.3	1:45	2:51	24½	257	391	447		1927	3962	5340	
	65-71	32	53	86.0	93.8	2:17	3:45	24½	175	338	393		1394	3354	4162	

Chemical Detail
Cement Analysis Paper No. [illegible]

Cement No.	I	II	III	IV	Yos. 1931 Avg.
Silica	21.86	22.38	23.04	23.26	23.02
Iron Oxide	2.25	2.54	2.59	2.11	2.09
Alumina	4.09	4.66	4.21	7.07	4.05
Calcium Oxide	66.54	66.11	65.15	63.26	66.31
Magnesia	1.64	1.48	1.59	1.42	1.66
Sulfur	2.00	1.97	1.90	1.75	1.52
Ignition Loss	1.50	.87	.81	.73	1.18
Uncombined Lime	1.00	.80	.60	.90	.50
Insoluble Res.	.22	.40	.28	.58	.21
Potential Compound Composition (Bogue's Method)					
C_4AF	6.84	7.63	7.87	6.41	6.35
C_3A	7.02	8.03	6.81	15.16	7.18
C_3S	65.61	56.00	52.06	25.76	55.75
C_2S	12.67	21.35	26.06	45.66	23.30
$CaSO_4$	3.40	3.35	3.23	2.97	2.58
Avg. Kiln. Disc. temp. °F.	2300	2300	2300	2300	
Avg. Treater temp. °	2500	2450	2450	2400	