BETTER CONCRETE THROUGH CHEMISTRY

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Concrete is one of our most versatile building tools and at the same time one of the most abused materials of construction. Despite this abuse, however, it does an outstanding job for the construction engineer.

Steel is manufactured in mills according to exacting specifications and can be checked by the various new techniques available as to its composition and strength before it is shipped to the job. In other words, it is a finished product before it is put in place. Concrete, on the other hand, is put in place as a mixture of ingredients and the end product, the hardened concrete, is developed on the job.

Concrete is made up of four basic materials; portland cement, sand, coarse aggregate and water. Individually, these materials have to meet certain specifications in order to insure that the resultant concrete will, when properly proportioned, develop the designed strength.

The American Society for Testing Materials has set up limiting specifications for the various types of portland cement. The manufacturers adhere to these requirements and furnish plant certifications to the effect that the cement will meet the specifications. Producers of coarse and fine aggregate will furnish these materials to meet the grading requirements, and minimum silt and organic contents as set forth in ASTM specifications. The purity of the water used is not generally a problem because water suitable for drinking purposes is considered satisfactory for use in producing concrete and is available in practically all areas.

The proper proportioning of these materials is important. Nationally recognized organizations, such as the American Concrete Institute and the Portland Cement Association, furnish tables and design information which can be used by the engineer to obtain the desired concrete strengths.

All of this is not enough, however, because it is impractical

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to control the hardening of the concrete in the field. Facilities are not available as they are in a steel mill for laboratory control of the mixture, and more important, the subsequent handling of the material as it becomes the finished product.

Concrete develops its strength by the hydration of the portland cement. It is a complex reaction which develops products that bind the mix together in a solid mass. No attempt will be made in this presentation to explain this reaction, but suffice it to say at this time that it is a chemical reaction which starts as soon as the cement and water come in contact. Once this reaction is started there is no turning back and starting over again. The rate at which the concrete stiffens and hardens is governed primarily by time and temperature as is the case of most chemical reactions. Hence, the person responsible for placing the concrete must get it in the proper location before the reaction has proceeded to the point where the concrete becomes too stiff to move or handle. Often, unavoidable delays occur and, as a result, it will become necessary to reject the batch or add more water to the concrete in order to get it in place. Any addition of water automatically changes the mix design specified by the design enginer, and, as a result, lower-than-calculated strengths will be obtained. This fact is based on the work done by Duff Abrams some forty years ago and since substantiated beyond a doubt by many other investigators (1)(2)(3). Mr. Abrams showed that the strength of the concrete in the plastic range varied inversely with the water cement ratio. The higher this ratio, the lower the strength.

More than enough water to hydrate the portland cement is added to every concrete mix for the practical purpose of making it possible to place it. The practical man on the job has to place this concrete in many difficult locations and under adverse conditions. He may have a network of heavy reinforcing steel to get it by and around. He may have breakdowns of equipment or forms which delay the placing. He may be working in below zero weather or with temperatures running around 100° F. Hence, it is obvious that any steps that can be taken to reduce the water/cement ratio of a given mix while at the same time maintaining plasticity will improve the strength. Chemistry has played an important part in making possible the use of minimum water/cement ratios.

Over twenty-five years ago, several manufacturers interested in the production of cement and concrete started investigating the possibility of applying their knowledge of dispersing techniques to portland cement. One of the first applications was a highway in the state of Massachusetts where a dark, concrete pavement was desired. Up to this time, the use of materials such as carbon black to produce dark concrete had met with little success because the color was not uniform and the strengths suffered due to a large increase in water requirement. It was found, in the course of investigations, that certain materials such as lignosulfonic acids and their salts had a pronounced effect on the fluidity or plasticity of portland cement pastes, mortars and concrete, plus the fact that they were good dispersants for carbon black. In other words, less water was required, as much as 15-20% less, to produce an equivalent plasticity to that of a non-treated mixture, and in turn less carbon black was required for a given degree of color. In accordance with Abrams' water/cement ratio law, this resulted in higher concrete strengths for the same cement content. There was, however, another factor introduced by the use of these materials. They increased the setting time of the portland cement. A concrete which normally obtained its initial set in four to five hours was found to require six to seven hours for initial set. This was a mixed blessing. For example, this delay could be of inestimable value on the job where difficult placing problems existed or high atmospheric temperatures prevailed. On the other hand, it proved to be a distinct disadvantage under low temperature conditions or where early form removal was desirable.

This was a challenge to the chemists and they went to work on the development of two types of admixtures. One suitable for use in controlling the delay in the intial set of the concrete and one that would not alter the setting time from that of the non-admixtured concrete; both materials to have the desired water reducing, plasticizing properties. As a result of research by the leading manufacturers in this field, we now have available these two types of materials which are becoming widely used in the concrete field. Both fall into two basic types of chemicals; lignosulfonic acids and their salts and hydroxylated carboxylic acids and their salts. At the Third Pacific Area national meeting of the American Society for Testing Materials, a very complete symposium was held on water reducing and initial set retarding admixtures of these types (4). Data and opinions were presented by specifiers, consumers, concrete producers and admixture producers which indicated these types of admixtures to be a definite factor in the production of quality concrete.

The fact that these materials reduce the basic water requirements of the concrete mix means that the consumer is getting an increase in the design factor of safety if no change is made in the mix design. On the other hand, the proper redesign of the concrete mix will result in economies in construction. Since the design engineer is primarily interested in the concrete developing a certain strength, it is generally accepted practice to specify a minimum strength requirement at twenty-eight days. It is true that some engineers still specify mix proportions which include a minimum cement factor and maximum water content, but this does not necessarily insure the proper strength. Despite the fact that the materials used in concrete meet certain specifications, it is a well-known fact that the strength produced from materials of different sources may vary as much as 100%. Hence, it is best that the designer specify strength and leave the mix proportions to the concrete engineer, who is better qualified to take advantage of the available materials to produce quality concrete.

If the job requires retardation, the concrete engineer can use the proper admixture addition rate to obtain the desired setting time. He not only has his own experience to draw on, but also that of the admixture manufacturers and their research laboratories.

Initial retardation of the concrete generally means extending the time of initial set at least two hours beyond that normally found in the same concrete under identical conditions, but with no retarding admixture present. This time of intial set is determined by means of a Proctor Penetration apparatus in accordance with ASTM Designation C 403 (Fig. I). Initial set is considered to have taken place when the concrete will resist a pressure of 500 pounds per square inch as applied by the penetrometer. At this point it is considered impossible to move or further consolidate the concrete by vibration, and it is also often referred to as the "vibration limit."

The length of time of initial retardation can be varied to suit the job requirements by adjusting the addition rate of the admixture. (Fig. II). The admixtures are generally supplied by the manufaturers in a liquid, ready-to-use form, thus making it simple for the concrete producer to satisfy the needs of the engineer.

The early strength, sometimes up to one day, is lower for initially retarded concrete than for regular concrete of the same cement factor, plasticity and under identical conditions. After two days of

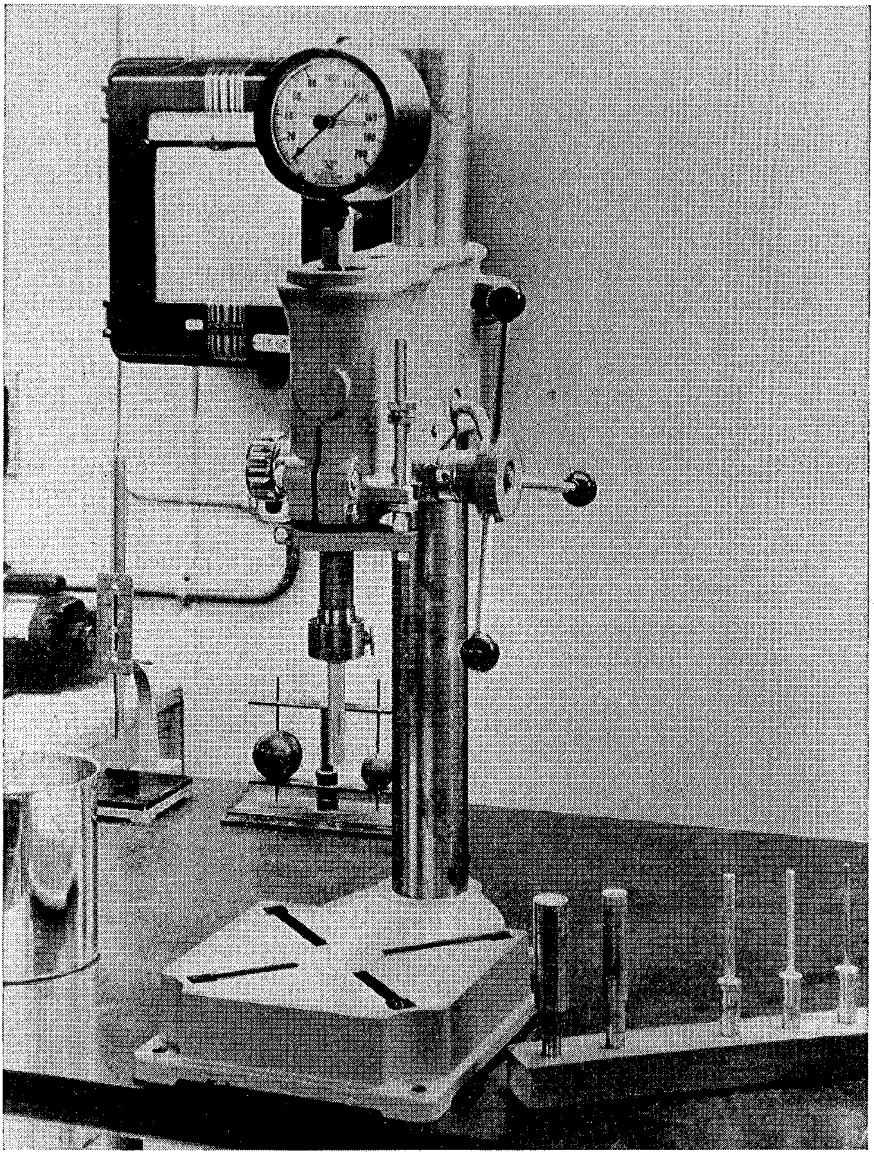

FIGURE I.—PROCTOR PENETROMETER.

curing, however, the strength of the initially retarded concrete surpasses that of the plain concrete, and maintains this advantage at all later ages. This strength increase generally amounts to 10-18%, depending on mix design and other related factors.

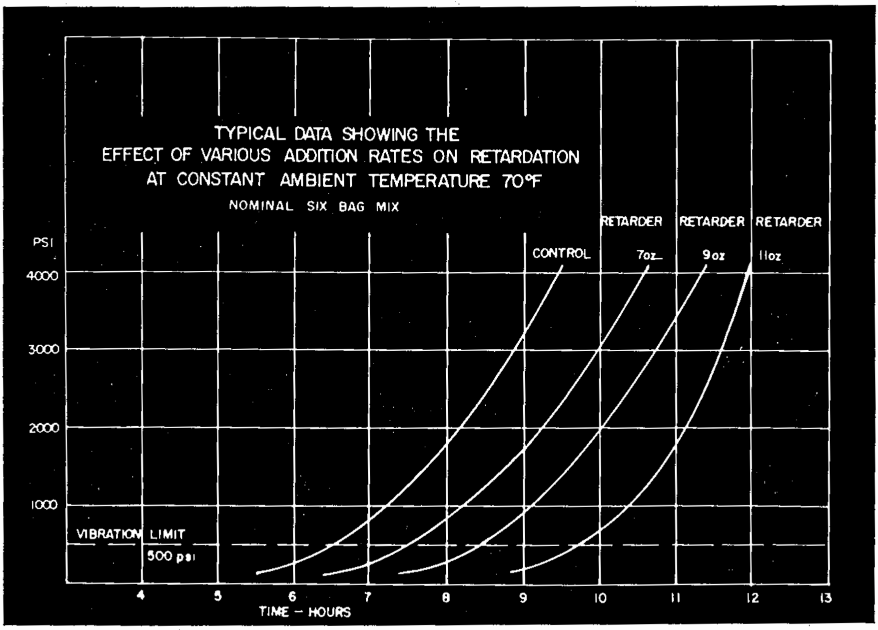

FIGURE II.—TIME OF SET-ASTM DESIGNATION C 403 VARIABLE ADDITION RATE OF RETARDER.

Initial retardation enables the contractor to properly place concrete under conditions which would otherwise seriously affect the quality of the job. High temperatures cause rapid setting of the concrete and interfere with the proper finishing. Also, too rapid a rate of hardening may cause cracking as in the case of bridge decks. In such an instance it is important that the concrete remain plastic until all of the concrete is in place and there will be no more deflection due to loading the supporting members. Another instance where rapid setting can cause trouble is in prestressed beams. It is essential that the concrete remain plastic during the period of vibration so that it will not be broken away from the stressed steel and lose the very important bond to steel that must be developed.

The water reducing type of admixture is basically the same as the initial retarding admixture except that it has been modified chemically to eliminate the retarding influence. A fixed addition rate is generally recommended and is based on the cement factor.

Both types of admixtures have many common factors. They increase the plasticity of the mix by reducing the interparticle attraction of the cement, thus in effect lubricating the mix. This action reduces the water requirement of the mix anywhere from 10-20%, depending on the mix design and materials used. As has been pointed out, this reduction in water is reflected in increased compression strength. The over-all quality of concrete is indicated by compressive strength and, therefore, better bond strength, greater flexural strength, higher durability, increased abrasion resistance, less bleeding, and lower permeability are some of the benefits that may be derived from the use of these materials.

Perhaps the best known admixture for concrete is that which introduces air in the mix. This type of admixture is relatively new compared to the water reducing materials, but its use has grown rapidly because of the spectacular results obtained. About 1940 it was discovered that concrete containing entrained air had superior resistance to the deterioration due to freezing and thawing cycles. This immediately started researchers on the road to finding out the optimum quantity of air, the size of the bubble, the spacing, and the methods of introducing the air. It was found that the air produced by either of two chemicals, a sulfonated hydrocarbon containing a catalyst and a wood rosin by-product, was the most effective. Other chemicals introduced air in the desired percentages, but they invariably seriously affected the resultant strength and/or did not increase the durability. Further research on this problem, principally by members of the U. S. Bureau of Reclamation staff, has turned up the fact that these two materials are unique in the size of the bubble produced, the angle of contact, and the surface film. In normal concrete there are approximately four million of these bubbles per cubic inch and they average less than 100 microns in diameter. Other types of air of larger bubble diameter, lower contact angle, or lower film strength are not satisfactory. At the same total air content, there may be only about 400,000 bubbles per cubic inch (5).

Air entrainment is not limited to climates where freezing and thawing cyles are prevalent. Research has shown that definite advantages may be obtained where the concrete is in contact with alkali salts (6). The salts that enter the concrete under these conditions are destructive. The growth of such crystals in the concrete exerts a terrific pressure just the same as the freezing of water. Concrete being a rigid material will break when this pressure exceeds its inherent strength, but if there are the tiny air voids interconnected by capillaries as in air entrained concrete to absorb some of this pressure, the concrete has several hundred per cent greater chance of surviving.

In addition to the benefits which air entrainment imparts to the durability of concrete, there are other important factors to consider. Air entrainment lubricates the concrete mix by providing ball bearings for the aggregate to roll on (Fig. III). Hence, the water/cement

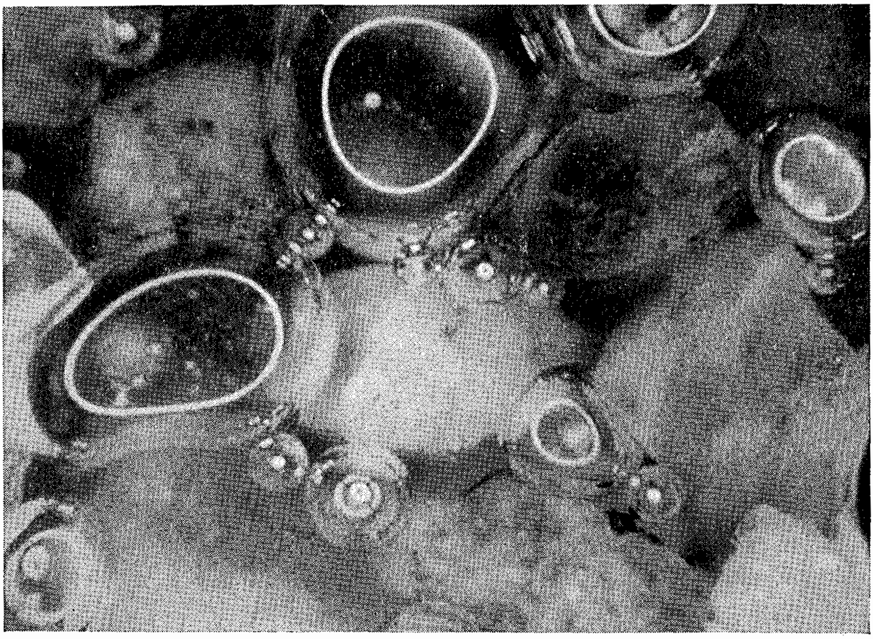

FIGURE III.—ENTRAINED AIR IN SAND MIX (65× MAGNIFICATION).

ratio of the mix can be and should be reduced to maintain designed plasticity. This reduction in water generally compensates for any strength loss that may be introduced by substituting air for solid material in mixes containing 6 sacks of cement or less. One manufacturer provides an agent containing a catalyst which further reduces any tendency toward strength loss. It should also be noted that when making comparisons between non-air entrained concrete and air entrained concrete, it is essential that the actual cement factor be maintained. Since air is, in a sense, a fifth ingredient of the concrete mix, it is necessary to reduce the quantity of one of the other ingredients to compensate for this addition. This is generally done by reducing the sand volume an amount equivalent to the approximate air content minus the water reduction (7).

Other uses of chemicals in concrete include materials to accelerate the setting of the cement. Such materials have particular application in cold weather work because as with all chemical reactions temperature plays an important role in the rate of the hydration of the cement. In cold weather this reaction is slowed down considerably unless suitable precautions are exercised. The use of warm aggregates and mixing water plus heated or insulated forms helps this situation, but it is often desirable to add an accelerator to insure proper setting. The most widely used material for this purpose is calcium chloride. It is important, however, that such material be used with discretion since excessive quantities can cause too fast a reaction. Normally the addition rate is limited to 2% by weight of the cement except in rare cases, and often 1% is sufficient with heated materials (8).

Recently materials have been developed by the chemists which greatly aid in the repair of concrete. There are two general types of these materials. One is a synthetic latex type emulsion which can be mixed with portland cement, aggregate and water to provide a mix that will bond to practically any material and has the same properties and appearance as concrete. The material can be featheredged and used to repair either thin or deep surfaces as well as broken sections. It is a "ready-to-use" product which will generally re-emulsify if exposed to water, but is also available in a composition that will not reemulsify or soften in the presence of water. This latter type is particularly recommended for use in areas exposed to weathering.

The other bonding or repair material is a two component mixture which is generally applied as a glue to bond the newly placed concrete to the old or as a surfacing material. It is basically expoxy resin which is relatively expensive and difficult to apply, but these disadvantages may well be justified where the protection of the concrete from such deleterious materials as acids and alkalies is of prime importance. It is a very strong bonding agent, far exceeding the strength of concrete, and must be properly plasticized to avoid excessive strains.

Many times reference is made to concrete produced by the Romans in making their aquaducts. This is used as an illustration as to how much more lasting this concrete seems to be than our present day material. We could produce this type of concrete, but because of our present day concepts no one would accept it. The reason is that the Romans were not in a hurry. The concrete they made was not put into service for a long time, possibly several years, after it was placed. It had plenty of time to adequately cure and develop strength. The cementitious material was a slow hydrating type and gained strength very slowly compared to our standards. We, on the other hand, demand that the concrete be ready to take the full designed load almost as soon as it is placed. In order to meet these requirements the cement chemists have adjusted chemical compositions and fineness, admixture chemists have provided hydration aids and water reducing materials, but despite all of this we still haven't been able to duplicate the effect of time. We are making progress, but the old adage to the effect that the longer it takes to produce a material the longer it will last, still holds true to a certain extent.

The cement and concrete chemists are never idle. New ideas are being investigated daily. The future of the application of chemical admixtures in portland cement concrete is unlimited. Our research people are continually finding new types of admixtures which, although perhaps not as glamorous as those we read about for cosmetics, are of vital importance to the concrete consumer. Every concrete structure is in a sense a monument, and it must be built to last.

Then next few years will bring completely new chemical admixtures to make portland cement concrete even more versatile and efficient than it is at the present time.

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