Concrete Lining System for the Continuous Tunnel Boring Machine

by

Gail S. Kelley

Submitted to the Department of Civil and Environmental Engineering
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Abstract

The Continuous Tunnel Boring Machine (CTBM) is a joint project between the Civil and Mechanical Engineering Departments at MIT. As an integral part of the tunneling process, a slipformed lining is extruded directly behind the cutter head; the forward thrust for the tunneling machine is provided by the pressure of the concrete as it is pumped into the slipform. This work examined what is required of the concrete, both in terms of the functioning of the machine and the tunnel lining structure.

As opposed to typical concrete construction where the properties of the hardened concrete are the primary concern, in the case of the CTBM, the properties of the fresh concrete are of equal, if not greater, importance. Thus the properties and behavior of fresh concrete were discussed with particular emphasis on testing and quality control. The main requirement of the concrete was found to be a very high early strength, according to previous work, a strength of 30 MPa may be required at four hours. In addition, the concrete must be workable enough to placed by pumping. Various proprietary cements were reviewed since it is unlikely that such a high early strength can be obtained with ordinary Portland cement. In addition, the advantages and disadvantages of both chemical and mineral admixtures were discussed.

One potential problem that came to light during this work was the possibility of thermal cracking of the tunnel lining. The mechanisms behind thermal cracking and how it relates to the hydration of cement were thus examined in some detail.

Thesis Supervisor: Herbert H. Einstein
Title: Professor

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I would like to acknowledge the help, particularly the very constructive criticism, given to me by my advisor Professor Herbert Einstein, during the writing of this thesis.

I would also like to acknowledge four other people from whom I learned more than I realized:

- Bob Penny, who taught me the value of a challenge
- Dan Walker, who taught me the value of a person
- Professor Jim Diekmann, who taught me the value of the word plausible
- Tom Hunter, who taught me you have to love the game

To Maureen, Drew and alot of other people

And so we go on to where the mountains reach the sky

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Chapter 1

Introduction

1.1 Objective of this research

This research is being done in conjunction with a continuous tunnel boring machine (CTBM) being developed by the Mechanical Engineering Department at MIT. As an integral part of the tunneling machine, an extruded slipformed lining is created immediately behind the tunnel face. The novel feature of the system is that the forward thrust for the tunnel boring machine is provided by the pressure of the concrete as it is pumped into the slipform. The purpose of this research is to determine what is required of the concrete, both in terms of the working of the tunnel boring machine and for the long term durability and structural stability of the tunnel.

Considerable research on slipformed tunnel linings was done during the late 1970's and early 1980s. A large part of this work focused on the properties and behavior of the concrete. Although this work was reviewed closely, very little of it was strictly applicable. In particular, the cements they used in their experiments appear to be no longer manufactured in this country. Since the behavior of a concrete is largely a function of the cement, their results and conclusions are not entirely useful. In addition, much of their work, (Parker, 1973) for example, was done assuming that the concrete would only need to provide self support, i.e. it was not supporting a ground load. For some of this work therefore the strength requirement was that the concrete achieve a compressive strength of 3.4 MPa (500 psi) in 1 1/2 hours.

This is significantly less than what it is anticipated will be involved with the CTBM (potentially as high as 30 MPa in 4 hours.)

This work is intended to provide a basic overview of the properties and behavior of concrete as it will be used with the CTBM. Much of the material is taken from textbooks on concrete and manuals on concrete construction and is considered to represent either common knowledge or generally accepted opinions. There are an enormous number of variables involved in both the manufacture and use of concrete. Out of necessity much of the research currently being done in concrete is being done on very specific aspects of its behavior or under very restrictive test conditions. In addition, much of the research is actually done on cement paste; it is not entirely clear how some of this research relates to concrete as a construction material. Since the results obtained from research on both cement and concrete often appear to be contradictory, citing examples tends to confuse rather than clarify the issue. Consequently, specific research is not cited unless it is directly applicable to the CTBM.

1.2 Requirements of the Concrete

The two most important requirements of the concrete for the CTBM is that it be pumpable and attain a high early strength. The principles involved in formulating a pumpable mix are fairly well understood. Mix design is not an exact science however, it is more a combination of experience, basic physics and trial and error. Most of literature on mix design, in particular mix design for pumping, is given in very general terms as rules of thumb. The importance of making adjustments after testing trial mixes is highly stressed.

Design of high early strength mixes is quite a bit more scientific and since it represents an important commercial opportunity, quite a bit of work has been on the chemistry of high early strength cements. There is also a considerable amount of work being done on the development of chemical admixtures to accelerate strength development. Most of the research with regards to actual construction has been done in the area of highway pavement repairs. In general construction, the advantages of a concrete with high early strength usually do not justify the additional cost. A recently completed five year Federal Highways study referred to as the Strategic Highway Research Program (SHRP) looked at various aspects of high early strength concrete design. A number of research projects were undertaken at both state universities (North Carolina State University, University of Arkansas, University of Michigan) and through private engineering/testing companies (Construction Technology Laboratories). The reports which came out of these projects are available from the Transportation Research Board (TRB). Quite a few of these projects were aimed at evaluating test methods (a 28-day compressive test result is not particularly useful for evaluating concrete one would like to open to traffic in 4 hours). Along the same lines, other projects attempted to determine what the performance criteria actually should be.

A number of these tests did however evaluate different mix designs and cements. In particular, SHRP contract C-205 *Mechanical Behavior of High Performance Concrete* evaluated a number of different mixes. One problem with these tests is that they were primarily evaluating mixes on the basis of what they had determined to be their performance requirements. They established three categories of mix design: Very Early Strength (VES), High Early Strength (HES) and Very High Strength (VHS). Of the three, only VES, which specified 21 MPa (2500 psi) at 4 hours was close to the CTBM requirements; the HES specifications were for 35 MPa (5000 psi) at 24 hours, VHS was for 70 MPa (10,000 psi) within 28 days. The SHRP investigators evaluated mixes used by several state transportation departments (Ohio DOT, Iowa DOT) for early opening pavement repairs. These mixes are based on Types I and III Portland Cement and used various amounts of admixtures including water reducers, superplasticizers and accelerators. They also evaluated mixes based on two proprietary cements: Rapid Set from CTS Cement Manufacturing Company and Pyrament from Lone Star Systems. Given that they were designing these mixes for a specific requirement, their results do not necessarily indicate the limits of what is possible as far as high early strength. However Paul Zia, the principal investigator on one of the projects noted that they were only able to produce concrete which had a strength of 21 MPa concrete by using Pyrament cement. They found it difficult to make workable concrete of such high early strength even with Type III (high early) Portland cement [Zia, 1994]. It should also be noted that workability for a highway application basically means that it must be able to get the concrete out of the truck, a mix that is going to be pumped would have to be significantly more fluid.

The concretes used in these tests all had very high cement contents ranging from 650 to 1000 pounds per cubic yard. On some of the installations, there were problems with thermal cracking, this was a due to the very high heat of hydration these mixes produce. As is typical with most pavements, these installations were jointed (saw cut) at 4 meter (12 foot) intervals. Cracking problems developed when the jointing was delayed and significant tensile stresses had built up. The mixes using the proprietary cements required less cement to achieve the same strengths, as a result they also experienced less temperature rise [Whiting, 1994].

1.3 Construction Process

In evaluating requirements for the CTBM an attempt was made to find similarities with other construction processes. The CTBM proposal however is fairly unique. Vertical slipforming (i.e. silos, chimneys, building cores) is similar in concept but quite a bit less demanding as far as the concrete requirements.

In vertical slipforming, the form, work decks and finishing scaffolds are supported by rods embedded in the concrete, the entire assemblage is raised by jacks which climb the rods in small (typically 1 inch) increments. These rods extend down into the hardened concrete however, at the time it emerges from the slipform the concrete must only be capable of supporting the weight of the concrete above it, approximately 50 psi. Typically the forms are 4' high pieces of plywood; advance rates will depend on the type of work (how much reinforcing steel there is) but are usually not more than 24 inches per hour. At this rate, the concrete is at least two hours old when it leaves the form, a two hour strength of 50 psi is attainable without any special accelerating techniques.

There is no motivation for using high early strength cements since the advance rate is typically limited by the rate at which the rebar can be placed. The advance rate must however be matched with the rate at which the concrete is setting, typically the goal is to have the concrete start setting 12 to 18 inches from the bottom of the form. If the concrete is setting too slowly, it will not be sufficiently strong when it leaves the form. If it is setting too fast however, it will generate a considerable amount of friction against the forms. The forms are normally designed with a batter of approximately 1/16 inch per foot to minimize the drag on the concrete. Friction can in fact present a problem, the plywood is usually faced with a layer of polyethylene, if the friction is too great and/or the plywood is of poor quality, there can be bubbling or tearing of the polyethylene or delamination of the plywood.

Vertical slipforming relies heavily on visual observation. The point at which the concrete is setting is determined by driving a rod down through the fresh concrete by hand, the degree of set of the free standing concrete is determined by thumb pressure, overall concrete quality is judged by appearance. One significant problem in vertical construction is that the setting of the concrete can be affected by the ambient temperature, humidity, sunlight and wind. Advance rates may thus have to be adjusted because of changes in the weather. Since the temperature and humidity within a tunnel are fairly constant some of these problems will be eliminated.

Horizontal slipforming which is used in the construction of curbs and median barriers, is again a very different process from both the CTBM and vertical slipforming. The form used in a slipforming machine is typically about 2 feet long and advance rates may easily be 100 feet an hour. Consequently, the concrete must be self-supporting almost immediately. The strength in this case however is from mechanical interlock of the aggregate rather than the result of a chemical set. Very low slump ("no-slump") concrete is used and the form is tapered to force compaction.

Chapter 2

Concrete Fundamentals

The objective in concrete mix design is to obtain a product that will perform according to certain predetermined requirements. Typically these requirements are that the concrete be as economical as possible, attain a certain strength, and have adequate workability. For the CTBM, the requirements are more specifically that the concrete be pumpable and have a high early strength.

Based on previous work [Darrow, 1992], [Marsh, 1993] an advance rate of 4 meters per hour has been selected. Given the proposed slipform length of 12 meters, the concrete will have to support ground approximately 3 hours after being placed. Finite element modeling [Bobet, 1994] has estimated that the concrete leaving slipform may have to support stresses as high as 27 MPa in sand and 32 MPa in clay. These stresses may be slightly high due to approximations in the model, it is probably more realistic to use 25 and 30 MPa for sand and clay respectively. Nevertheless, these are extremely high values for three hour strengths, the rate at which the concrete develops strength may thus be a limiting factor in the advance rate of the machine.

Typically, one of the key considerations in mix design is that cement costs much more than aggregate. Therefore it is desirable to use the smallest amount of cement consistent with the requirements of the concrete. Using a high cement content also increases the chances of cracking due to high heat of hydration and drying shrinkage. When strength (or durability) considerations require a low water to cement (w/c) ratio it is generally achieved by lowering the water content by using water reducing admixtures rather than increasing the cement content. In the case of the CTBM however, the early strength required may be such that both a low w/c ratio and a very high cement content are required. Consequently, as will be discussed in a later chapter, special precautions may be needed to avoid cracking.

When discussing the strength development of concrete it is important to understand the distinction between setting and strength development. It is also important to understand the difference between the setting of cement and the setting of concrete. Although the term "setting" implies solidification of the plastic cement paste, the initial and final set times of cement are essentially arbitrary values used for quality control. If all other variables are held constant, a rapid setting cement will produce a concrete which sets faster than a normal cement. There is no direct correlation between the set times of the cement and the set times of the concrete however. Furthermore, final set represents the beginning of strength development, the compressive strength of concrete at final set being only on the order of .7 MPa (100 psi).

2.1 Setting of Cement

Concrete is produced by mixing anhydrous cement powder, water and aggregate of various sizes. Typically the aggregate is divided by size into coarse and fine, coarse aggregate is that larger than 4.75 mm, fine aggregate is that smaller than 4.75 mm. Although the terms sand and gravel nominally refer to naturally occurring (as opposed to crushed) aggregate, they are often used synonymously with fine and coarse aggregate. Most concrete is about 75% aggregate by volume. It is the reaction between the water and the cement which is responsible for the production of concrete however.

In terms of its mechanical behavior, concrete can be represented as a composite material made up of a coarse aggregate phase and a mortar phase, the mortar being made up of the hydrated cement, voids and fine aggregate. When freshly mixed, concrete closely approximates the behavior of a Bingham (non-Newtonian) fluid. Over time the cement hydrates and since the hydration products are less dense than the original cement grains they eventually fill part or all of the space originally occupied by the mix water. The hydration products bond to each other as well as to the aggregate particles to form a solid rock-like mass.

If these hydration reactions happen too quickly there can be problems with having enough time to transport and place the concrete. If these reactions happen too slowly however subsequent construction processes may have to be delayed. As a result, ASTM C 150, *Standard Specifications for Portland Cement*, defines two essentially arbitrary setting times for Portland cements, initial set and final set. To ensure that a cement is in fact hydrating normally, ASTM C 150 requires initial set to be at least 45 minutes and final set to be no more than 375 minutes. These times are typically determined by a Vicat Needle according to the procedures given in ASTM C191.

The Vicat test is carried out in two stages: in the first stage, the proportions of cement and water which produce paste of standard consistency are determined by a series of tests on a trial and error basis. The standard consistency is an arbitrary characteristic, it is obtained when a 300 gram cylindrical plunger penetrates between 34 and 36 millimeters into a 40 mm deep mould. The second stage involves the determination of the setting times by penetration tests carried out in regular intervals on a sample of standard consistency. The tests again use a 300 gram mass but measure the penetration with needles. Two different needles are used, the needle for determining initial set is 50 mm long with a diameter between 1.08 mm and 1.18 mm. Initial set occurs when the needle penetrates only 35 mm. The needle for final set has the same diameter but has a bell shape piece 5 mm from its end. When this bell shape piece ceases to leave an impression it means the penetration is less than 5 mm and the paste is considered to have reached final set.

An alternative method for the assessment of setting times, used mostly in the U.S., is the Gilmore test. The Gilmore test is also based on needle penetration and requires the paste to be of standard consistency. The needle for testing initial set has a diameter of 2.12 mm and supports a mass of 113.4 grams, the needle for testing final set has a diameter of approximately 1 mm and supports a mass of 454 grams. The initial and final setting times correspond to the times at which the paste has stiffened

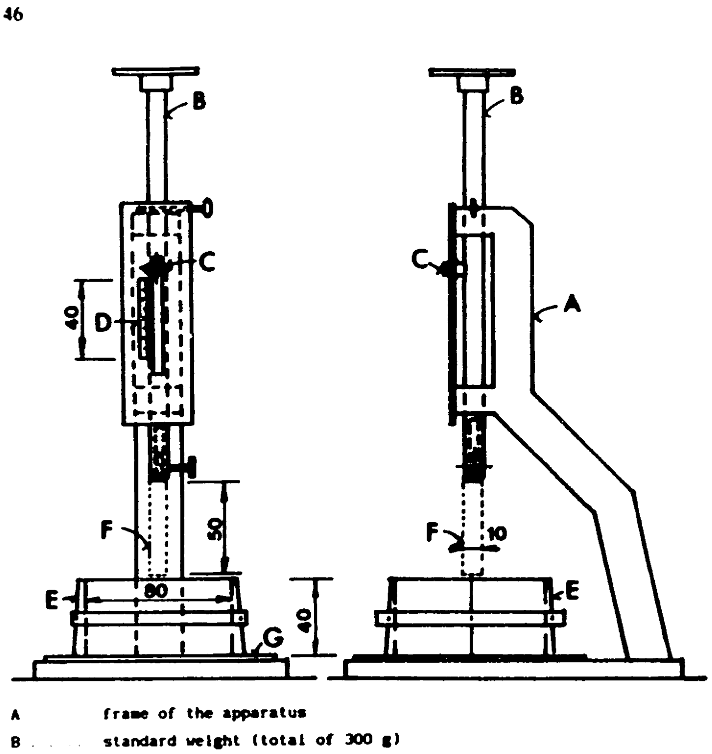


Figure 2-1: Apparatus for ASTM C 191, Vicat Test [Mindess and Young, 1981]

sufficiently to support the respective needles without any appreciable indentation.

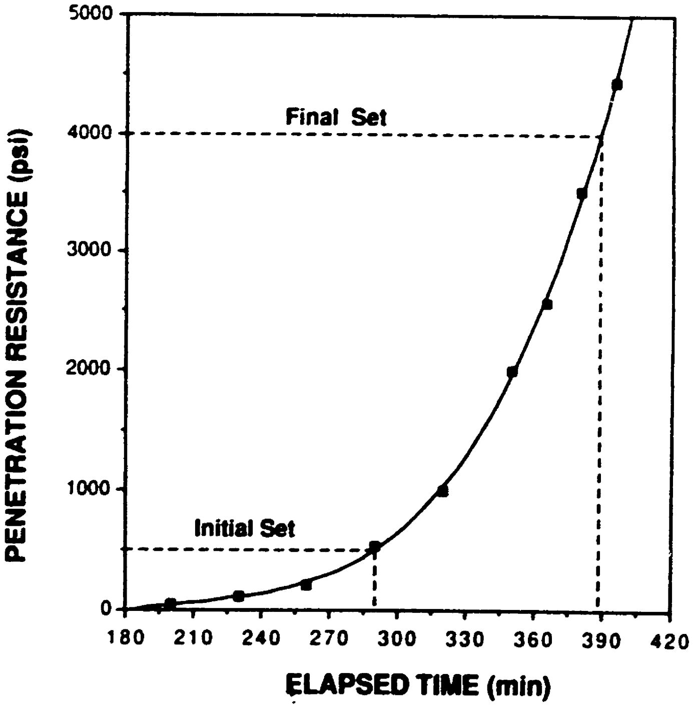
The setting times indicate that a certain amount of hydration has taken place. As measured by either test however, final set corresponds approximately to the beginning of the hydration of the tricalcium silicate, the major compound in cement, the paste therefore has very little strength at this time. Once the tricalcium silicate starts to hydrate, the reaction continues rapidly for several weeks. The progressive filling of the void spaces in the paste with the reaction product results in a decrease in porosity, this is turn causes a decrease in permeability and an increase in strength. The hydration process is discussed in detail in Chapter 4.

2.2 Setting of Concrete

These penetration tests measure properties of the "bulk paste" unmodified by the presence of aggregate. Determination of the setting times of concrete is more complicated because the presence of aggregate influences the setting time of the paste and the concrete overall. As discussed in Chapter 5, part of the paste in concrete changes from "bulk paste" into interfacial paste of different properties and composition. The setting times obtained from tests on pastes cannot be reliably applied to concrete; a concrete may lose all its useful workability before the the initial set of the paste or it may have attained no useful strength at a time corresponding to the final set of the paste. In addition, a given paste may produce concrete with widely varying set times when combined with different aggregate.

In order to overcome difficulties with extrapolating from the setting times of the paste, a penetration test on the mortar fraction of concrete was developed; the specifications for this test are given in ASTM 403, *Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance.* The concrete to be tested is first wet sieved to remove all aggregate over 4.75 mm and then compacted by vibration or rodding. Needles with bearing areas ranging from 16 and 645 mm^2 (.025 to 1 in ^{2}) are inserted into the fresh concrete and the force required to produce a penetration of 25 mm within 10 seconds is recorded. Penetration resistance is calculated by dividing the penetration force by the area of the needle; a series of tests is done at regular intervals and a curve of time versus penetration resistance is plotted. The initial and final setting times are taken from the curve as the times which correspond to penetration resistances of 3.5 MPa (500 psi) and 27.6 MPa (4000 psi). These values are somewhat arbitrary, nevertheless, initial set corresponds approximately to the point at which the concrete has become unworkable, i.e. placing, compacting and finishing by normal means would be difficult beyond this point. Final set indicates that hydration has progressed far enough for the mix to attain a minimum of useful and measurable strength.

The mortar obtained by wet sieving will not be completely representative of the actual mix however. In addition, it should be noted again that the values obtained from the testing are penetration resistance, not compressive strength. The penetration tests are actually measuring shear resistance. Although they do in fact indicate that a certain amount of hydration has taken place and thus there is a decrease in porosity, there is not a direct correlation with compressive strength. As noted



Plot of Penetration Resistance Versus Elapsed Time and Hand Fit Curve Used to Determine Times of Setting

Figure 2-2: Plot of Penetration Resistance, ASTM C 403

previously, at final set concrete only has a strength on the order of .7 MPa (100 psi).

2.3 The Water to Cement Ratio

One of the key parameters in determining the strength of the concrete is the ratio of the mix water to the cement, commonly referred to as the w/c ratio. For concrete to stiffen, harden and develop strength, there must be a chemical reaction between the cement and the mixing water. The critical feature of this reaction is that if the volume of water is 1.2 times the volume of cement all of the originally water filled spaces can be filled with hydration products. Because cement has a specific gravity of about 3.15, a ratio of 1.2 by volume is equal to .4 by mass. If the mass of the water is more than .4 times the mass of the cement, there will be still be mix water available after all of the cement hydrates. Over time this water will evaporate leaving empty space or voids which are referred to as capillary voids or capillary pores. If the original ratio is lower than .4 some of the cement will always remain unhydrated but in theory all of the originally water filled spaces will be filled with hydration products.

There is sometimes confusion about these numbers, in particular there is a misconception that the mass of the water only needs to be .2 times the mass of the cement for complete hydration. In actual fact, only slightly more than .2 times the mass of the cement (in other words 20 %) chemically combines with the cement. (The two major compounds in cement are tricalcium silicate and dicalcium silicate, tricalcium silicate requires 24% by mass chemically combined water, dicalcium silicate requires 21%.) The calcium silicates hydrate to form a gel which has about 26% porosity however. When the gel is formed, the pores within the gel must be full of water. These are referred to as gel pores and as opposed to the capillary pores mentioned above, they are part of the gel structure. The water in these pores may be lost later as the concrete dries but it must be available as the gel is formed. Some of this water is absorbed on the surface of the gel, some of it is between the layers of the gel.

The amount of water needed for hydration is thus equal to the amount which will combine chemically plus the amount held in the gel pores. As noted above, the amount of water chemical combined with calcium trisilicate is 24% or .24 grams/gram of cement, the amount of water held in the gel pores held in the gel pores is .18 grams/gram, thus the total water for hydration of tricalcium silicate is .42 grams/gram of cement. Since tricalcium silicate is the major compound in cement, this is a fairly good approximation for cement as well.

The amount of water in the original mix is also significant because it provides the space needed for hydration. When 1 cm^3 of cement hydrates, the hydration products occupy approximately 2.2 cm^3. Thus approximately 1.2 times by volume (.4 by mass) water is necessary so that there is enough space for the hydration products. The capillary porosity of a paste is a reflection of how much of the space originally filled by mix water was subsequently filled with hydration products. For a typical cement, the capillary porosity P_c of the paste is given as:

$$P_c = w/c - .36\,\alpha \text{ cm}^3/\text{gram of cement}$$

where α is the degree of hydration. Thus a w/c ratio of .36 will result in a capillary porosity of zero at complete hydration.

For zero porosity, therefore, a w/c ratio of .36 is required, whereas for complete hydration a w/c ratio of .42 is required. If a w/c ratio of .42 is used, all of the cement will be able to hydrate but in theory there will be some capillary porosity because the hydration products do not fill all of the space originally occupied by the water. In actual practice, water will be physically lost from the paste by evaporation, absorption by formwork, etc. In addition, it is usually impossible to get 100% of the cement to hydrate. A w/c ratio of .4 is typically used as the best approximation of "complete hydration" with the understanding that there may be a small amount of unhydrated cement and some capillary porosity.

In actual practice, water will be physically lost from the paste by evaporation, absorption by formwork, etc. In addition, it is usually impossible to get 100% of the cement to hydrate. A w/c ratio of .4 is typically used as the best approximation of “complete hydration” with the understanding that there may be a small amount of unhydrated cement and some capillary porosity.

There is nothing inherently wrong with having unhydrated cement however. A lot of modern “high performance” concretes are made at w/c ratios well below .4 and have large amounts of unhydrated cement. Since the strength of concrete, like most solids is dependent on its porosity, the objective is to minimize the amount of pore space (voids) in the hardened concrete. Thus the original space to be filled is kept as low as possible to ensure that it will all be filled with hydration products. Similarly, in order for concrete to have high early strength, it must rapidly generate hydration products to reduce the amount of pore space. Strength generation will be more rapid if again a low w/c ratio is used since there will be less pore space to be filled.

Most ordinary strength concrete has a w/c ratio above .4 however. A higher w/c ratio means that the concrete flows more easily, thus making it considerably easier to pour and compact. The typical concrete specified in residential construction is 3000 psi which may have a design w/c ratio of .68. 5000 psi concrete which is sometimes used in more heavily loaded commercial buildings, may require a design w/c ratio on the order of .48 [Komatsu and Panarese, 1990]. It should be noted however that these are design w/c ratios - one of the biggest problems in ensuring concrete quality is that water may be added at the site, thus producing concrete with a higher w/c ratio than specified.

2.4 Setting versus Strength

As noted above the setting times of concrete can be measured by a penetration test. The value for final set indicates the time at which hydration has progressed enough to produce a measurable amount of strength. In a typical Portland cement, strength development essentially starts at the time of final set, thus in order to have high early strength it is helpful to use a cement which sets rapidly. Strength development is not linear however, in particular it is difficult to make predictions about subsequent strength development based the final set. Portland cement is actually made up of four compounds, two aluminates and two silicates, each of which hydrates at a different rate. The strength development up to the point of final set is primarily due to the hydration of the two compounds present in the smallest percentages, the aluminates, the later strength development is due to the hydration of the silicates. As specified by ASTM C150, the amount of each compound present within a given type of Portland cement can vary somewhat, two cement pastes of nominally the same composition may have slightly different setting and strength patterns. The strength development of the same paste with different amounts or types of aggregate can also vary.

In particular, with respect to setting and strength, if a cement is formulated with a high percentage of tricalcium aluminate, or if the hydration of this compound is accelerated, the set times of the cement will be accelerated. Unless, however, there is also an acceleration of the silicates, there will be not be a significant increase in early strength development. In other words, the cement will achieve the value of strength corresponding to initial set earlier than normal but will not develop further strength until the silicates begin to hydrate as usual.

Predictions of strength development are even more difficult with proprietary cements. These are cements whose setting and strength behaviors depend on some compound other than the four main Portland cement compounds. Typically, the formulations are held as trade secrets and the data available from the manufacturer as far as strength testing may be somewhat limited. These cements may be formulated to have a rapid set, i.e. develop a small amount of strength very quickly. This does not necessarily mean that they will develop significant strength any quicker than a normal cement however. In addition, although the promotional literature for a cement may give strength data as of certain points, i.e. 4 hours, 24 hours, 7 days, there is no way however to infer other values from this data. Furthermore, many of these cements are promoted as patching materials; testing is done on concrete with very small aggregate and a very high cement content, these formulations may not be appropriate for a structural concrete.

With proprietary cements in particular, it is thus essential that testing be done on the actual job materials and under proposed job conditions for placing and curing. This holds for all cements however. The behavior of any cement may be influenced by an almost infinite number variables and their interactions. Some factors such as temperature and w/c ratio are obvious. Other factors which are less obvious but potentially very significant are the order in which admixtures are added, the rate at which mixing is done (the energy imparted to the mix) and the temperature and humidity at which the cement has been stored.

Chapter 3

Portland Cement

Portland cement belongs to a class of materials known as hydraulic cements; these are materials which react with water and harden to form a water-resistant product. The primary ingredients of Portland cement are calcium and silica; calcium and silica oxides are heated to 1600 °C (2550 °F) at which temperature they combine to form calcium silicates. Limestone (calcium carbonate) is the most common source of the calcium oxide although other forms of calcium carbonate such as chalk, shell deposits and calcareous muds are sometimes used. Iron-bearing aluminosilicates are typically used as the primary source of the silica; clays and silts are preferred since they are already in a finely divided state, in addition the silica is more reactive than that found in quartz or sandstone. The location of cement plants is often determined by the availability of calcium since it is usually easier to obtain silica.

In descriptive terms, the reactions which take place in a cement kiln are as follows:

$$\text{Limestone} \rightarrow CaO + CO_2$$
$$\text{Clay} \rightarrow SiO_2 + Al_2O_3 + Fe_2O_3 + H_2O$$
$$CaO+SiO_2+Al_2O_3+Fe_2O_3 \rightarrow$$
$$3CaO{\cdot}SiO_2 \;/\; 2CaO{\cdot}SiO_2 \;/\; 3CaO{\cdot}Al_2O_3 \;/\; 4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$$

Cement is formed by a process of clinkering (partial melting) as opposed to fusion (complete melting); only about a quarter of the charge in a cement kiln is in liquid form at any time. The output of the kiln, called clinker is basically a mix of four minerals: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). Its exact composition will depend both on the composition of the raw materials and the rate at which the liquid cools. After leaving the kiln, the clinker is ground to particles on the order of 1 - 75 μm. A small amount of gypsum (calcium sulfate) is added during the grinding to control the setting properties of the cement. A final blending of cements is typically done to average out minor differences in chemical composition that occur during manufacture.

Although there are several different types of Portland cement specified by ASTM, the differences in formulation are slight. They all contain approximately 50-60% tricalcium silicate, 20 - 25% dicalcium silicate, 10% tricalcium aluminate, 5-8% tetracalcium aluminoferrite and 3-4% calcium sulfate dihydrate (gypsum). The silicates make up about 75% of the cement and are responsible for long term strength development; they hydrate to form calcium hydroxide and a fibrous calcium silicate gel referred to as C-S-H. The aluminate and aluminoferrite hydrate to form a compact needle-like calcium aluminate trisulfate called ettringite. Ettringite is primarily responsible for the setting and early strength of cement, however on a volume basis it contributes considerably less than C-S-H to the strength of the cement. In addition, it can cause problems with durability and abnormal setting. Aluminum and iron have a mineralizing effect in the production of cement however, they allow the calcium silicates to form at lower temperatures than they would in pure silica-lime systems. Small amounts of alumina and iron oxide are often added (particularly in the western US) if there is not enough in the raw mix.

3.1 Cement Composition

The chemical compounds in cement are typically written in a ceramics' industry shorthand. In this notation, a compound is considered to made up up of oxides (i.e. CaO, SiO_2, Al_2O_3, Fe_2O_3), carbon dioxide (CO_2) and sulfur trixoide (SO_3) each of which is designated by a single letter. The common oxides and compounds found in cement are shown in the tables below.

OXIDES

SiO_2	S	(Silicon Dioxide)
Al_2O_3	A	(Aluminum Oxide)
Fe_2O_3	F	(Ferric Oxide)
MgO	M	(Magnesium Oxide)
CO_2	$\bar{C}$	(Carbon Dioxide)
SO_3	$\bar{S}$	(Sulfur Trioxide)
H_2O	H	(Water)

COMPOUNDS

$3CaO{\cdot}SiO_2$	C_3S	(calcium trisilicate)
$2CaO{\cdot}SiO_2$	C_2S	(calcium disilicate)
$3CaO{\cdot}Al_2O_3$	C_3A	(tricalcium aluminate)
$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$	C_4AF	(tetracalcium aluminoferrite)

Although it is possible to determine the amount of each compound in a cement by direct analysis, it is a fairly expensive process. For routine analysis, the percentages of the different oxides are determined and the amount of each compound is then calculated from stoichiometry. The equations used for this calculation, the Bogue equations, are shown below. Since the results are only approximate, they are referred to as the potential compound compositions.

BOUGE EQUATIONS:

$\% \ C_3S = 4.071\ C - 7.600S - 6.718A - 1.430F - 2.850S$

$\% \ C_2S = 2.867S - 0.7544C_3S$

$\% \ C_3A = 2.650A - 1.692F$

$\% \ C_4AF = 3.043F$

3.2 Reactivity of the Cement Compounds

The rate at which concrete develops strength is a function of the reactivity of the compounds in the cement. This in turn is primarily a function of the crystal structures of the compounds. Because they are formed under high temperature and non-equilibrium conditions the crystal structures are far from perfect. The impure forms of C_3S and C_2S, referred to as alite and belite respectively, both contain small amounts of magnesium, aluminum, iron, potassium, sodium and sulfur. Alite is very reactive, it is built around SiO_4 tetrahedra, calcium ions and oxygen ions with the oxygen concentrated on one side of a calcium ion. This arrangement, combined with the impurity atoms, leaves large structural holes that account for the high lattice energy and reactivity. The structure of belite is also irregular however the holes are smaller than in C_3S, consequently C_2S is less reactive. The C_3A and C_4AF contain considerable amounts of impurities including magnesium, sodium, potassium, and silica. The crystals of these compounds also have large structural holes which result in compounds with very high reactivity.

The reactivity of the various compounds can be compared by looking at calorimetric curves which measure the amount of heat evolved (heat of hydration). C_3A is significantly more reactive than the other compounds; after three days its heat of hydration is more than three times as much as C_3S and more than fifteen times as much as C_2S. Cement with high a C_3A content will develop strength quickly; cement with a high C_2S contents will develop strength quite slowly.

3.3 Fineness of the Cement

The reactivity of a cement with a given composition will be a function of its fineness (particle size distribution); because finer cements have more surface area, they react more quickly. To get an accurate determination of the cement fineness it is necessary to do a complete analysis of the particle size distribution by sedimentation. Since this is fairly expensive, a relative measure of fineness is usually obtained from a surface area analysis. Specifications for this are given in ASTM C 204, *The Blaine Air Permeability Method.* The results are expressed in terms of m^2/kg, although this does not provide any information about the particle size distribution, it does give a good indication of the reactivity of the cement.

The rate of strength development can be controlled to some degree by adjusting the fineness of the cement. Typical particles size distribution for Type I (standard) and Type III (high early strength) cements are shown below:

% Passing:	Type I	Type III
7.5 um	22 %	42 %
15 um	46	66
30 um	74	88
45 um	88	97

Depending on the cement composition, changing the surface area from 320 to 450 m^2/kg can increase the 1 day compressive strength of a cement mortar by 50 to 100 % [Mehta and Monteiro, 1993]. However the increase in concrete strength will be somewhat lower than that of the corresponding mortar since there are other factors involved. Concrete strength is discussed in more detail in Chapter 12.

It is generally agreed that cement particles larger than 45 μm are difficult to hydrate and particles larger than 75 μm may never hydrate completely, as a result, fineness is sometimes reported as the residue on the #200 (75 μm) and #325 (45 μm) sieves [Mehta and Monteiro, 1993].

3.4 Types of Portland Cement

Knowing the composition of a cement, it is possible to predict its properties. Furthermore, cements with desired properties can be produced by adjusting the composition. ASTM C 150, *Standard Specification for Portland Cement* includes standards for the following types of cement:

Type I: for use when the special properties of other types are not required. There are no limits on any of the four principal compounds (C_3S, C_2S, C_3A and C_4AF)

Type II: for general use, especially when moderate sulfate resistance or moderate heat of hydration is required. Since C_3A and C_3S have high heats of hydration, C_3A is limited to 8 percent. There is an optional limit of 58% combined C_3S and C_3A which applies when moderate heat of hydration is required and heat of hydration test data is not available.

Type III: for use when high early strength is required. The C_3A is limited to 15 percent, to ensure that the high early strength is not due mainly to its hydration. As a result, the high early strength is primarily due to the higher specific surface (550 m^2/kg Blaine versus 330 to 400 for Type I cement.)

Type IV: for low heat of hydration. C_3S and C_3A are limited to a maximum of 35 and 7 percent respectively. A minimum of 40% C_2S is required and the 7 and 28-day heats of hydration are limited to 60 and 70 cal/gram respectively.

Type V: for use when high sulfate resistance is required. There is a maximum limit of 5% on the C_3A because one of the hydration products in cements which contain more than 5% C_3A, is monosulfoaluminate. Monosulfoaluminate is unstable when exposed to a sulfate solution, conversion of the monosulfate to ettringite is generally associated with expansion and cracking.

ASTM C150 also contain specifications for Types IA,IIA and IIIA cement which are the standard types with air entraining clinker interground. There is little demand for these cements however since air-entraining admixtures provide better control over the amount and distribution of air. In the United Kingdom, there are four main types of cement: ordinary (BS 12), rapid-hardening (BS 12), low heat (BS 1370) and sulfate-resisting (BS 4027). These correspond to the ASTM types I, III, IV and V respectively. The Canadian standards are given by the Canadian Standards Association (CSA) as CSA 10, 20, 30, 40 and 50 corresponding to Type I, II, III, IV and V.

As shown in the table below, the required compositions for each of the ASTM types is given as a fairly wide range; the ASTM specifications are aimed at ensuring the cement has certain properties rather than a specific composition. It should also be noted that the existence of an ASTM specification does not guarantee the commercial availability of a particular cement type. Low heat cement (Type IV) is no longer made in the US because mineral admixtures are a less expensive way to control temperature rise. When heat of hydration is a consideration, Type I or II cement is usually blended with a pozzolan. In addition, Type V cement is only available in certain parts of the country where there are high levels of sulfate in the groundwater [Mindess and Young, 1981]. More than 90% of the hydraulic cements produced in the US are Types I and II, approximately 5% are Type III and the rest are special cements such as oil-well cements. Many cements are formulated so that they meet the specifications for both Type I and II [Mehta and Monteiro, 1993].

TYPICAL COMPOUND COMPOSITION OF CEMENT

TYPE	C_3S	C_2S	C_3A	C_4AF
I	45-55	20-30	8-12	6-10
II	40-50	25-35	5-7	6-10
III	50-65	15-25	8-12	6-10
V	45-50	25-35	0-4	10-20

3.5 Blended Cements

The five ASTM types all consist mainly of the four major clinker compounds - C_3S, C_2S, C_3A and C_4AF in varying proportions. There a number of other Portland cements which are formed either by adding other materials to the clinker or by forming other compounds during burning. These cements are sometimes referred to as modified Portland cements since they are still basically calcium silicate cements. Typically these modified cements are designed to produce either higher strength concrete (particularly at early ages) or higher quality (more durable concrete.)

Specifications for blended cements are covered in ASTM C595, *Specification for Blended Hydraulic Cement.* These are cements which have a large amount of either a pozzolan or blast furnace slag interground with the clinker or separately ground and then added to the clinker. Although specifications for several cements are given, these cements are rarely used in the U.S., typically pozzolans and slag are added to the concrete as it is being batched. This allows for flexibility in the amount of pozzolan added, it also avoids having a separate storage silo for the blended cement.

Specialty cements formulated for high early strength will be discussed in Chapter 6, blast furnace slag and pozzolanic materials will be discussed in Chapter 11.

Chapter 4

Hydration of Cement

One of the most important things to understand about concrete is that it does not harden due to drying. The hardening of concrete is actually the result of chemical and physical processes that take place between cement and water. In order to understand the properties of concrete it is necessary to understand the hydration processes.

The actual mechanism by which cement hydrates is not completely understood. Two possible mechanisms are through-solution and topochemical. In through-solution hydration the anhydrous compounds in cement dissolve to their ionic constituents. Hydrates are formed in solution; due to their low solubility they eventually precipitate out. There is thus a complete reorganization of the original compounds.

In topochemical or solid-state hydration the reactions take place directly at the surface of the cement grains, without the compounds going into solution. It appears that through-solution is dominant initially but at later stages the hydration products start to fill the available space and ionic mobility becomes limited. Hydration then tends to shift to a topochemical process.

The chemical reactions involved in the hydration of the cement compounds have been worked out in part by studying the hydration of the pure compounds. This assumes that the hydration of each compound in cement takes place independently of the others. Although this is not completely valid since there are interactions between the hydrating compounds, i.e. there is competition for sulfate ions, it reasonably accurate for most cements.

4.1 Hydration of the Aluminates

As discussed in previous chapters, cement is made up of calcium aluminates and calcium silicates. Since the aluminates hydrate much faster than the silicates they are largely responsible for the stiffening (loss of consistency) and setting (solidification) characteristics of a Portland cement paste. C_3A in isolation reacts vigorously with water; crystalline hydrates such as C_4AH_{13} and C_2AH_8 are formed quickly and large amounts of heat are liberated. The reaction is shown below; when it occurs in cement, the formation of the calcium aluminate hydrates causes an extremely rapid set known as "flash" set.

it is referred to as according to the reaction:

$$C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8$$

Neither of these initial hydrates are stable and they subsequently convert to C_3AH_6 (hydrogarnet) via the reaction:

$$C_4AH_{13} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H$$

This is the same conversion that causes the disruption of the paste in high alumina cement, because the high rate of heat liberation causes a large temperature rise, the conversion occurs extremely rapidly. Because of the disruption of the paste, C_3A hydrating by itself does not develop substantial strength.

Gypsum in various forms (dihydrate, hemihydrate, anhydrite) is added to cement to curb the C_3A hydration and prevent flash setting. Typically, it is interground with the cement clinker. The mechanism by which the gypsum retards the C_3A is not well understood, according to one theory, the solubility of the C_3A is depressed in the presence of sulfate ions. When the C_3A hydrates, it reacts with the sulfate ions according to the equation:

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32}$$

where $3C\bar{S}H_2$ is the dihydrate form of gypsum. The reaction product, $C_6A\bar{S}_3H_{32}$, is the calcium sulfoaluminate hydrate commonly called ettringite after the naturally occurring mineral of the same composition. It is sometimes written as $C_3A{\cdot}3C\bar{S}{\cdot}H_{32}$ to emphasize the reactants. Ettringite is only stable while there is a large supply of sulfate available however, i.e. when the molar ratio of $C\bar{S}H_2$ to C_3A is above 3. In most cements with more than 5% C_3A, the sulfate is consumed before the C_3A is completely hydrated. After the sulfate is depleted, the concentration of the aluminate in solution will begin to rise as the C_3A and C_4AF continue dissolving. Eventually, the ettringite will become unstable and transform to a calcium sulfoaluminate hydrate which contains less sulfate. The reaction is show below:

$$2C_3A + C_6A\bar{S}_3H_{32} + 4H \rightarrow 3C_4A\bar{S}H_{12}$$

This second product, $C_4A\bar{S}H_{12}$, is called tetracalcium aluminate monosulfate-12-hydrate or monosulfoaluminate, it is sometimes written as $C_3A{\cdot}C\bar{S}{\cdot}H_{12}$. If monosulfoaluminate comes into contact with sulfate ions, ettringite can be re-formed via the reaction:

$$C_4A\bar{S}H_{12} + 2C\bar{S}H_2 + 16\ H \rightarrow C_6A\bar{S}_3H_{32}$$

This is why portland cements with high C_3A contents are susceptible to sulfate attack.

As the ettringite forms, it creates a diffusion barrier around the C_3A and thus slows down hydration. This barrier breaks down when the ettringite converts to monosulfoaluminate and allowing the C_3A to react further. Both the initial formation of ettringite and the conversion to monosulfate are exothermic and evolve considerable amounts of heat. There is a peak in heat evolution during the first 15 minutes of hydration and another peak when the ettringite converts to monosulfoaluminate. Conversion to monosulfoaluminate will occur in most cements within 12 to 36 hours depending on how much gypsum there is, with more gypsum, it remains stable longer. Monosulfoaluminate may also form initially in place of the ettringite if sulfate ions are not being supplied rapidly enough, a certain concentration of sulfate ions is required for the formation of ettringite.

4.2 Calcium Aluminoferrites

The reactions of the C_4AF are similar to those of the C_3A. Depending on the sulfate concentration, the hydration of C_4AF may produce either $C_3A(F)\bar{S}_3H_{32}$ or $C_4A(F)\bar{S}H_{18}$ which have variable chemical compositions but structures similar to ettringite and monosulfoaluminate respectively.

The reactions are slower and evolve less heat however. C_4AF never hydrates rapidly enough to cause flash set and gypsum retards C_4AF hydration even more than C_3A hydration. The iron content of the C_4AF tends to vary somewhat, with higher iron contents it is more reactive, it is also more reactive if it was formed at a lower temperature. Cements which are low in C_3A but high in C_4AF are resistant to sulfate attack which means that the monosulfoaluminate formed does not convert back to ettringite. The monosulfoaluminate has iron oxide as a partial replacement for alumina, for some reason this appears to prevent it from converting to ettringite.

4.3 Alumina / Sulfate Ratio

The various setting phenomena can be significantly affected by an imbalance in the alumina/sulfate ratio. Normally, cement paste will remain workable for about 45 minutes, it will start stiffening as water-filled spaces begin to fill with ettringite. The paste becomes less workable 1 to 2 hours after the addition of water and begins to solidify at 2 to 3 hours. If the concentrations of aluminate and sulfate ions in solution are high however, large amounts of ettringite are formed rapidly. This can cause a considerable loss of consistency within 10 to 45 minutes and solidification of the paste in 1 to 2 hours. This behavior is characteristic of high C_3A cements which have large amounts of gypsum in a highly soluble form; it is also the basis for many rapid setting cements. When either the amount of C_3A is extremely high or not enough gypsum was added to the clinker, the C_3A will hydrate extremely rapidly to form large amounts of monosulfate and calcium aluminate crystals. As noted above this is referred to as flash set, there is a large evolution of heat and poor ultimate strength.

4.4 Hydration of the Silicates

Although the sulfate ions contributed by gypsum have a retarding effect on the aluminates, they increase the solubility of the silicate compounds and thus have an accelerating effect on them. Hydration of the silicates, C_3S and C_2S, produces two principal reaction products. One is actually a family of calcium silicate hydrates, referred to as C-S-H, which are structurally similar but vary widely in both their calcium to silica ratio and their chemically combined water content. It is primarily the structure of the C-S-H which determines its properties however, the compositional differences are usually not significant. C-S-H is poorly crystalline and forms a porous solid which exhibits the characteristics of a rigid gel. In the early literature, it was sometimes referred to as tobermorite gel after a naturally occurring mineral which appeared to have the same structure. SEM analysis has shown that the crystal structures are actually quite different however and the name is no longer used. The composition of C-S-H can vary with the cement composition, w/c ratio, temperature and age of hydration. On complete hydration, the composition is approximately $C_3S_2H_3$, this is what is used for stoichiometric calculations. The other product of the silicate reactions, calcium hydroxide (CH), is a crystalline material with a fixed composition, $Ca(OH)_2$.

The hydration reactions of the two silicates are stoichiometrically similar but they differ in the amount of water required and the amount of calcium hydroxide formed. The stoichiometric reaction for a fully hydrated C_3S paste is:

$$2C_3S + 6H_2O \rightarrow C_3S_2H_3 + 3CH$$

For dicalcium silicate the reaction is:

$$2C_2S + 4H_2O \rightarrow C_3S_2H_3 + CH$$

The hydration of C_3S produces approximately 61% by weight $C_3S_2H_3$ and 39% CH whereas the hydration of C_2S produces 82% $C_3S_2H_3$ and 18% CH. The surface area and consequently the adhesive property of the hydrated cement paste are mainly due to the formation of C-S-H. As a result, the ultimate strength of a cement with a high C_3S content will be less than that with a high C_2S content. However since the durability of hardened paste to sulfates and acids is reduced by the presence of CH, high C_3S cement will be less durable then high C_2S cement in these environments; specifications for construction in acidic or high sulfate environments may limit the maximum C_3S content. The C_3S hydrates faster than C_2S however. In the presence of gypsum, fine particles of C_3S begin to hydrate within an hour of the water being added, the hydration of the C_3S is thought to be a factor in the time of final set and the early strength of the paste. The relatively quick rate of C_3S hydration is important in high early strength cements.

The hydration reaction of the silicates is most conveniently described using a calorimetric curve which measures the rate of heat evolution with time. The heat flow is proportional to the rate of reaction and is most easily measured for C_3S. C_2S hydrates in a similar manner but the reaction is much slower and less heat is liberated, consequently the calorimetric curve is harder to measure.

When C_3S in isolation is mixed with water there is a rapid evolution of heat lasting about 15 minutes. This is followed by a period of relative inactivity referred to as the dormant period or induction stage. This same dormancy occurs in cement pastes, the dormant period is the reason why concrete remains plastic for up to several hours. Initial set occurs after 2 to 4 hours, about the time the dormant period ends. The silicate begins to hydrate rapidly and reaches a maximum rate within 4 to 8 hours, this is also the maximum rate of heat evolution. By this time final set has been passed and hardening has begun. The reaction rate then slows down again and reaches a steady state within 12 to 24 hours.

The following physical processes occur: when the C_3S is first mixed with water, calcium and hydroxide ions are rapidly released from the surface of the C_3S grains; within a few minutes the pH rises to over 12. Although hydrolysis slows down quickly it continues at a greatly reduced rate throughout the dormant period. The dormant period apparently occurs because there needs to be a certain concentration of ions in solution before the hydration products can nucleate. When the calcium and hydroxide concentrations reach a critical value, the hydration products, CH and C-S-H begin to form and the C_3S reaction proceeds rapidly again.

Although the CH crystallizes out from solution, C-S-H tends to develop as a coating at the surface of the grain. As hydration continues, the coating becomes thicker and forms a barrier through which ions must diffuse to reach the unhydrated grain. Eventually movement through this layer determines the reaction rate, thus the hydration becomes diffusion controlled. Diffusion controlled reactions are typically quite slow and become slower as the thickness of the diffusion barrier increases. Consequently 100% hydration is approached asymptotically.

Although the hydration reactions are sensitive to temperature, the dependence varies according to the stage. Temperature sensitivity is strongest during the initial hydrolysis, the dormant period and the subsequent acceleration. During these stages, the reaction is under chemical and nucleation control. Once hydration becomes diffusion controlled, temperature will have less effect although the diffusion coefficient of the hydration barrier will vary slightly with temperature.

4.5 Heat of Hydration

The major compounds of portland cement (C_3S, C_2S, C_3A, C_4AF) are non-equilibrium products of high temperature reactions, they are therefore in a high energy state. In the presence of water, these compounds will react to acquire more stable, lower-energy states. The process is accompanied by the release of energy in the form of heat, i.e. the hydration reactions are all exothermic. The compounds hydrate at different rates according to different reaction stoichiometries however and they vary in both the rate at which they liberate heat and the total amount of heat they liberate.

Approximate values for the heat of hydration for a cement can be predicted from a weighted average of the individual components, i.e.

$$H = a\,(C_3S) + b\,(C_2S) + c\,(C_3A) + d\,(C_4AF)$$

where H represents the heat of hydration at a given time and a,b,c, and d are the heat evolved by 1% of the corresponding compound at that time. These values can be measured for each compound in isolation and used as a index of reactivity. Nevertheless, due to interactions with the other compounds, these measured values are typically slightly different for the compound when it exists as a component of cement. Multiple regression analysis has been done on cements of known chemical composition to come up with the following equations which are fairly accurate for cements of standard composition.

$$H_3day = 240\ (C_3S) + 50\ (C_2S) + 880\ (C_3A) + 290\ (C_4AF)$$

$$H_1year = 490\ (C_3S) + 225\ (C_2S) + 1160\ (C_3A) + 375\ (C_4AF)$$

H_3day is the total heat evolved is Joules per gram of cement after 3 days, H_1year is the heat evolved after 1 year, C_3S, C_2S, etc. refer to the percentage of each compound [Mindess and Young, 1981].

In general, when cement is mixed with water, there is a rapid heat evolution lasting a few minutes - it is thought that this reflects the heat of solution of aluminates and sulfates. This initial heat evolution ceases quickly, but again the reason is not very well understood. One theory is that the solubility of the aluminates is depressed in the presence of sulfate in the solution, another is that an insulating shell of hydration products develops around the cement grains.

For most cements, the next heat evolution cycle peaks after 4 to 8 hours of hydration. The peak corresponds to final set (complete solidification and beginning of hardening), its major component is the heat of formation of ettringite. Many researchers believe that there is additional dissolution of C_3S as well as some C-S-H formed during this period. Thus part of of the heat generated would be heat of solution of the C_3S and heat of formation of the C-S-H. For a typical cement approximately 50% of the potential heat is liberated within the first 3 days and 90 percent within the first 3 months of hydration.

4.6 Volume Changes During Hydration

An important aspect of the development of the paste structure is the decrease in porosity during hydration. All the hydration products of the cement compounds have lower specific gravities (greater specific volumes) than the cement compounds. Thus every hydration reaction is accompanied by an increase in the volume of solids, this is why the hydration products eventually fill all or most of the space originally occupied by the mix water. It is not only the potential volume changes that are significant however but also the way in which the changes occurs.

CH and C-S-H either grow around (engulf) solid particles or stop growing in a particular direction when they meet obstacles. Thus the hydration is not accompanied by an increase in the total volume of paste. The hydration products will only occupy the space that is available within the paste, the volume originally occupied by the mix water and cement particles. If this space is filled before complete hydration has occurred further hydration will virtually stop. It is quite different however when ettringite forms from C_3A and C_4AF, when their growth is impeded, ettringite crystals will make space for themselves. If the impediment is a rigid material, crystal growth pressures of up to 240 MPa (35 ksi) can develop.

In an unhardened paste the ettringite usually has enough space in which to form, if necessary it can make additional space by pushing aside obstructing cement grains. Once the paste has become rigid however, the space required for continued formation of ettringite must be created by expansion. In expansive cements, this expansion is restrained by rebar, thus creating the desired compressive stress. If they are not restrained, the internally generated expansions will create internal stresses that may crack and damage the paste. Ordinarily only small amounts of ettringite are formed after the paste has hardened so there is little expansion. If too much gypsum is added to the cement however large amounts of ettringite will be formed after the paste has set. The disruption of the paste may be sufficient to lower its compressive strength of the paste and cause severe cracking.

4.7 Sulfate Attack

Most soils contain some sulfate in the form of gypsum however since the solubility of gypsum in water at normal temperatures is limited, the amount of sulfate present is not harmful to concrete. When there are higher levels of sulfate, it is usually due to the presence of magnesium and alkali sulfates. Ammonium sulfate is frequently present in agricultural soils and effluent from the chemical industry and furnaces that use high-sulfur coals may contain sulfuric acid. Decaying organic matter in marshes, mining pits and sewer pipes often leads to the formation of H_2S which can be transformed into sulfuric acid by bacterial action.

There are two forms of sulfates attack. Which form occurs depends on the concentration and source of the sulfate ions (i.e. the associated cation) and the composition of the cement paste. In the first form, sulfate attack is manifested as expansion and cracking of the concrete, this increases the permeability of the concrete which accelerates the deterioration. The second, less common but potentially more destructive form manifests itself as a progressive loss of strength and mass due to deterioration of the hydration products [Mehta and Monteiro, 1993].

Deterioration limited to cracking is due to attack on the alumina bearing phases of the paste. Paste from portland cement with more than 5 % C_3A will contain most of the alumina in the form of the monosulfate hydrate, $C_3A{\cdot}C\bar{S}{\cdot}H_{18}$, if the C_3A content is more then 8 percent, the paste will also contain $C_3A{\cdot}CH{\cdot}H_{18}$. When these pastes come into contact with sulfate ions, the alumina containing hydrates react with the sulfate and calcium hydroxide to form ettringite, $C_3A{\cdot}3C\bar{S}{\cdot}H_{32}$:

$$C_3A{\cdot}C\bar{S}{\cdot}H_{18} + 2CH + 2\bar{S} + 12H \rightarrow C_3A{\cdot}3C\bar{S}{\cdot}H_{32}$$

$$C_3A{\cdot}CH{\cdot}H_{18} + 2CH + 3\bar{S} + 11H \rightarrow C_3A{\cdot}3C\bar{S}{\cdot}H_{32}$$

The mechanism by which ettringite formation causes expansion is not well understood, however ettringite is poorly crystalline and adsorbs considerable water as it forms. Many researchers feel the expansion is the result of the pressure exerted by the growing crystals. [Cohen and Mather, 1991].

The more severe form of sulfate attack occurs when the hydration products deteriorate and form gypsum. This causes a reduction of stiffness and strength, followed by expansion and cracking, eventually the material transforms into a noncohesive mass [Mehta and Monteiro, 1993]. Depending on the cation present (i.e. Na^+ or Mg^{2+}) either just the calcium hydroxide or both the calcium hydroxide and C-S-H may be converted to gypsum. With sodium sulfate, the reaction is as shown below:

$$Na_2SO_4 + Ca(OH)_2 + 2H_20 \rightarrow CaSO_4{\cdot}2H_2O + 2NaOH$$

The formation of sodium hydroxide as a by-product of the reaction ensures that the alkalinity of the paste remains high, as a result the C-S-H remains stable. With magnesium hydroxide attack however, calcium hydroxide is converted to the relatively insoluble and weakly alkaline magnesium hydroxide, thus the stability of the C-S-H is reduced and it is attacked as well. This results in even more serious deterioration of the paste, the equations are shown below ($CaO{\cdot}2SiO_2{\cdot}3H_20$ is C-S-H) :

$$MgSO_4 + Ca(OH)_2 + 2H_20 \rightarrow CaSO_4{\cdot}2H_2O + Mg(OH)_2$$

$$MgSO_4 + 3CaO{\cdot}2SiO_2{\cdot}3H_20 + 8H_20 \rightarrow$$
$$3(CaSO_4{\cdot}2H_2O){+}3Mg(OH)_2 + 2SiO_2{\cdot}H_20$$

Type V cement which has less than 5% C_3A is sufficiently sulfate resisting when ettringite forming reactions are the only consideration. However when high sulfate concentrations are present (on the order of 1500 mg/liter), Type V cement may not prevent the transformation of the hydration products to gypsum. Under these conditions, cements containing little or no calcium hydroxide appear to perform better. These include high-aluminaB cements, portland blast-furnace slag cements with more than 70 % slag and portland-pozzolan cement with at least 25 % pozzolan [Mehta and Monteiro, 1993]. The best defense against sulfate attack however is high quality concrete, specifically concrete with low permeability. This requires a high cement content, low w/c ratio and proper compaction and curing of the fresh concrete. Due to the requirement of high early strength, the concrete for the CTBM will probably have both a high cement content and a low w/c ratio. The pressure used in placing the concrete will provide some degree of compaction, additional compaction can to some extent be obtained by vibration. Cracking of the concrete, due to drying or thermal shrinkage presents a problem however since this allows sulfate containing water to penetrate the interior of the concrete.

It has been found that the rate of sulfate attack on a concrete structure with all faces exposed to sulfate water is less than if moisture is lost by evaporation from one or more surfaces [Mehta and Monteiro, 1993]. If evaporation is taking place, the sulfate containing water will be drawn through the concrete due to capillary action; there will be a gradual buildup of sulfates at the surface where the evaporation is occurring. In the case of the tunnel lining, the rate at which evaporation takes place will be a function of the environment within the tunnel, even at relatively high humidities however there will probably be evaporation at the interior surface of the liner.

Chapter 5

Structure and Properties of the Cement Paste

As a general rule, the properties of a material are a function of its structure, particulary its microstructure i.e. those features which cannot be seen without magnification. Because concrete has a heterogeneous, fairly complex structure, the theoretical structure-property relationships often used for other materials do not apply. Furthermore, although considerable testing has been done on both fresh and hardened concretes, the results are often contradictory. Nevertheless, there are a number of basic relationships that can be used to explain some of the properties of concrete.

At the macroscopic level, concrete is a composite material consisting of two major phases, coarse aggregate and mortar (hydrated cement paste and sand). As with many composites, the two phases are neither homogeneous nor are they homogeneously distributed with respect to each other. Unlike most composites, however, the structure of the paste phase changes with time as hydration progresses. Furthermore, even with a hardened concrete the paste surrounding the aggregate particles is different from that of the bulk paste when viewed at a microscopic level. The thin shell of paste surrounding the coarse aggregate is referred to as the transition zone. This interfacial region is typically only between 10 and 50 μm thick but it may be much weaker and more permeable than the bulk paste; consequently, it can have a considerable impact on the mechanical behavior of the concrete. The transition zone is what accounts for the fact that concrete shows inelastic behavior at about 40% of its ultimate strength, even though the components of concrete remain elastic until failure. It is also the reason why concrete fails at a considerably lower stress level than either of the two main components and why at a given cement content, w/c ratio and degree of hydration, cement mortar will be stronger than the corresponding concrete.

Neither the bulk paste nor the transition zones are homogeneous. They both contain a heterogeneous distribution of different types of solid phases, pores and microcracks. The various phases in the paste are not uniformly distributed nor are they uniform in size and morphology. Since strength and other related mechanical properties, are controlled by the microstructural extremes, not by the average microstructure, such inhomogeneities can be significant.

5.1 Composition of the Bulk Paste

Unhydrated portland cement is typically around 70% calcium silicate with the rest mainly calcium aluminates and calcium ferroaluminates. There is also a small amount of gypsum (calcium sulfate) which is added to control setting. When cement powder is mixed with water the calcium sulfate and calcium aluminate compounds go into solution very rapidly. Hydration starts within a few minutes as calcium, sulfate, aluminate and hydroxyl ions begin to combine. Crystals of a calcium sulfoaluminate hydrate called ettringite are the first to appear; calcium silicate hydrate and calcium hydroxide begin to form several minutes to a few hours later, depending on the cement. Depending on the alumina - to sulfate ratio of the cement, the ettringite typically becomes unstable after several days and decomposes to form monosulfate hydrate. In cements with a high calcium aluminate or low gypsum content, small amounts of calcium aluminates may be formed. A hydrated cement paste is thus made up of four principal solid phases:

- calcium silicate hydrate
- calcium hydroxide
- calcium sulfoaluminates/calcium aluminates
- unhydrated cement particles

5.1.1 Calcium Silicate Hydrate (C-S-H)

Calcium silicate hydrate, abbreviated as C-S-H, makes up 50 to 60% of the volume of solids in a completely hydrated paste. It is therefore the most important constituent in determining the properties of the paste. It is not a well-defined compound, the calcium to silicate (C/S) ratio varies between 1.5 to 2.0, the structural water content (H) varies even more. It is typically written with hyphens, to indicate that the composition is not fixed, in chemical equations it is written as $C_3S_2H_3$ since this is what it most closely approximates upon complete hydration.

Due to its variable composition it is not a well-crystallized material, it develops as a mass of nearly amorphous particles in the colloidal size range (less than 1 μm in any dimension). Its structure varies from fibers of various shapes to an intricate network or honeycomb morphology. A honeycomb morphology is particularly common when calcium chloride was used as an accelerator, it also forms when there is a high level of impurities. These varying morphologies are thought to be due, in part, to the varying compositions of the C-S-H.

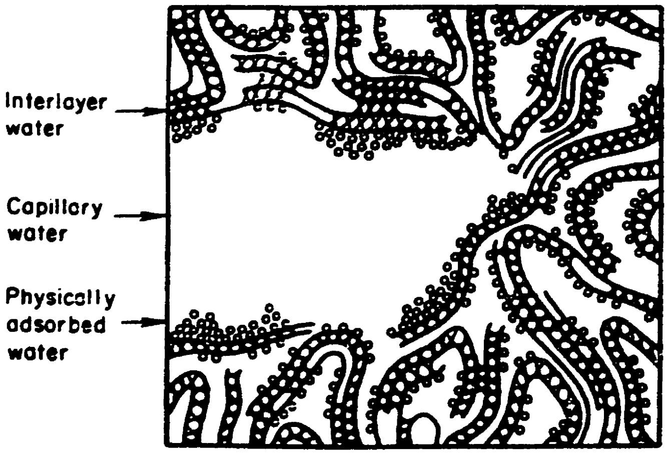
As a consequence of the small particle size of the C-S-H, hydrated cement pastes have very high surface areas. Measurements using physical adsorption of water vapor on vacuum dried calcium silicate pastes indicate that C-S-H formed at ambient temperatures has surface areas of 250 to 450 m^2/g (S_{H_2O}). This is three orders of magnitude higher than unhydrated cement grain which has surface of approximately .4 m^2/g. There is controversy over the determination of surface areas however since when nitrogen adsorption is used, surface areas (S_{N_2}) are much lower: 10 to 100

m^2/g [Mindess and Young, 1981].This is still a very high surface area compared to unhydrated cement however.

The C-S-H particles are so small that they can only be studied by electron-optical technique and even then cannot be complexly resolved. This fact, combined with its poor degree of crystallinity and variations in composition makes it a difficult material to study. Various models have been proposed to explain the structure and properties of C-S-H, the three major models being the Feldman-Sereda model, the Powers-Brunauer model and the Munich model. The difference between H_2O and N_2 adsorption data is one reason there are differences in the structural models, there are different interpretations of the discrepancy.

All three of the models consider C-S-H to have a layer structure, somewhat similar to a clay. A well defined clay mineral however will have fairly regular layers of silicoaluminate sheets stacked in a specific orientation. The spaces between the layers will be filled with water containing positive metal ions. The sheets are held together by comparatively weak attractions between the metal ions and residual negative charges on the sheets. In some clays the layers can expand to accommodate additional water, thereby expanding the crystal. The crystals contracts on drying since the interlayer water is lost and the layers collapse. This results in the large observed volume changes of some clays on wetting and drying.

In C-S-H, the layers are composed of calcium silicate sheets with calcium ions and water between them. Unlike a well-crystallized clay mineral however the sheets are randomly oriented due to variations in their composition and they do not fit together neatly. As a result the spaces between the sheets are irregular and vary considerably in size, some will be micropores, some will be capillary pores. Capillary pores are those which are large enough that pore water can behave as bulk (free) water, menisci are created as the pores are filled or emptied. In micropores, the adjoining surfaces are so close together that there is no bulk water, it is all bound to the C-S-H surface, albeit loosely. The water in micropores acts to keep the layers apart by exerting a disjoining pressure, when the sheets forming the micropores approach closely, they may bond due to van der Waals forces, they may also (less commonly) bond directly



Types of water associated with the calcium silicate hydrate. [Based on R. F. Feldman and P. J. Sereda, *Eng. J.* (Canada), Vol. 53, No. 8/9, 1970.)

In the hydrated cement paste, water can exist in many forms; these can be classified depending on the degree of ease with which water can be removed. This classification is useful in understanding the volume changes in cement paste that are associated with the water held by small pores.

Figure 5-1: C-S-H structure [Mehta and Monteiro, 1993]

by ionic-covalent bonds.

As water is removed from C-S-H rearrangement of the particles or layers is possible. C-S-H is in a high-energy state because of its extensive free surface. In general, it can be expected to respond to physical changes in a way that will decrease its surface area, thereby lowering its potential energy and increasing the ionic-covalent bonding between particles. Loss of water between layers or from surfaces increases the potential for bonding; drying appears to cause permanent changes in the structure as the result of increased bond formation.

5.1.2 Calcium Hydroxide

Calcium hydroxide (also called portlandite) makes up 20 to 25 percent of the volume of solids in a hydrated paste. In contrast to C-S-H, the calcium hydroxide is a well-crystallized compound with a definite stoichiometry, $Ca(OH)_2$. Although it tends to form as large crystals, it can vary in morphology being found as small equidimensional crystals, large flat plate crystals, large thin, elongated crystals and all variations in between. Its morphology is particulary affected by impurities, admixtures and the temperature of hydration. Although crystals large enough to be seen with the naked eye can sometimes grow inside voids, they do not grow as large within the body of the paste.

One of the significant features of calcium hydroxide is that it will only grow where free space is available. If it is obstructed by another calcium hydroxide crystal, it may stop growing or grow in another direction, if it encounters a cement grain, it may grow completely around it. Engulfing cement grains considerably increases the effective volume of the calcium hydroxide crystals.

Calcium hydroxide contributes to the strength of the paste in that it fills up the pores however it has much less surface area than C-S-H, consequently its contribution to strength is much less, in addition the crystals tend to cleave under shear [Mindess and Young, 1981]. Calcium hydroxide in hydrated portland cement can have an adverse effect on chemical durability; resistance to acidic solutions is lower because calcium hydroxide is more soluble than C-S-H, leaching of calcium hydroxide can provide an entry point for aggressive agents. Calcium hydroxide also considerably increases the susceptibility to sulfate attack.

5.1.3 Calcium Sulfoaluminates

The two primary calcium sulfoaluminates are the trisulfate hydrate, $C_6A\bar{S}_3H_{32}$ known as ettringite and the monosulfate hydrate, $C_4A\bar{S}H_{18}$. Although calcium sulfoaluminate compounds only occupy 10 to 15 percent of the solid volume of the hydrated paste they can have a significant effect on its behavior. During the early stages of hydration the sulfate/alumina ratio of the solution phase usually favors the formation of ettringite. In pastes of ordinary portland cement ettringite eventually transforms into the monosulfate hydrate. The presence of the monosulfate is what makes the concrete vulnerable to sulfate attack. If exposed to sulfate the monosulfate can convert back to ettringite and since ettringite crystals contain a large amount of water, this conversion can be accompanied by considerable expansion.

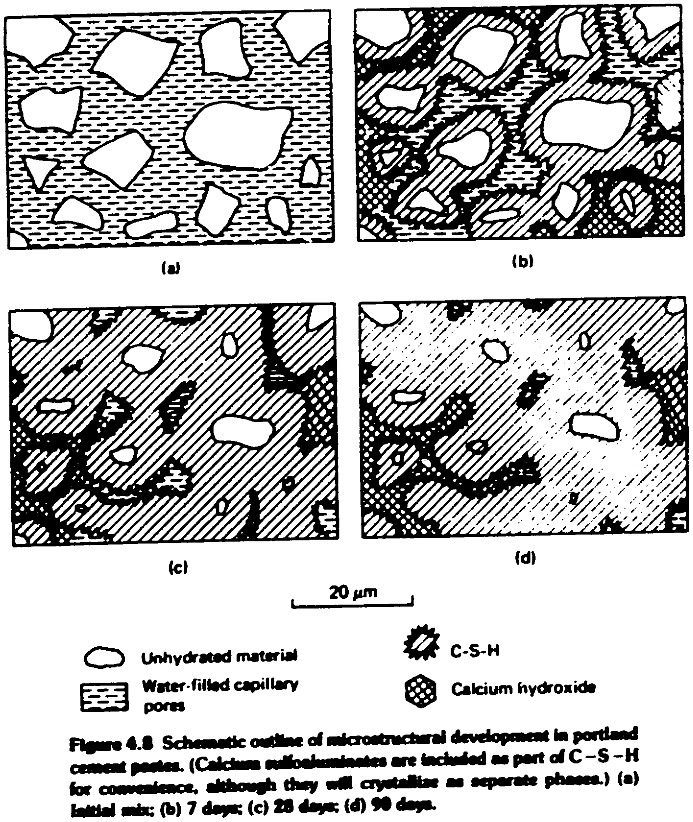


Figure 5-2: Idealized Representation of a Cement Paste Microstructure [Mehta and Monteiro, 1993]

The shape of the ettringite crystals depends on both the available space and the supply of available ions. In ordinary portland cement they typically form as long, slender needles. In expansive or regulated-set cements where large quantities form rapidly, they tend to form as stubby, intergrown crystals, pastes of these cements have their early microstructure dominated by ettringite crystals closely packed together.

5.1.4 Unhydrated Cement Grains

Unhydrated residues of the cement grains may exist even in well-hydrated cements; occlusion by calcium hydroxide may prevent complete hydration or there may be insufficient free space or water within the paste. The hydration process is such that first the smaller particles dissolve, then the larger particles shrink. Although it depends on the size distribution, particles larger than 75 μm typically never hydrate completely.

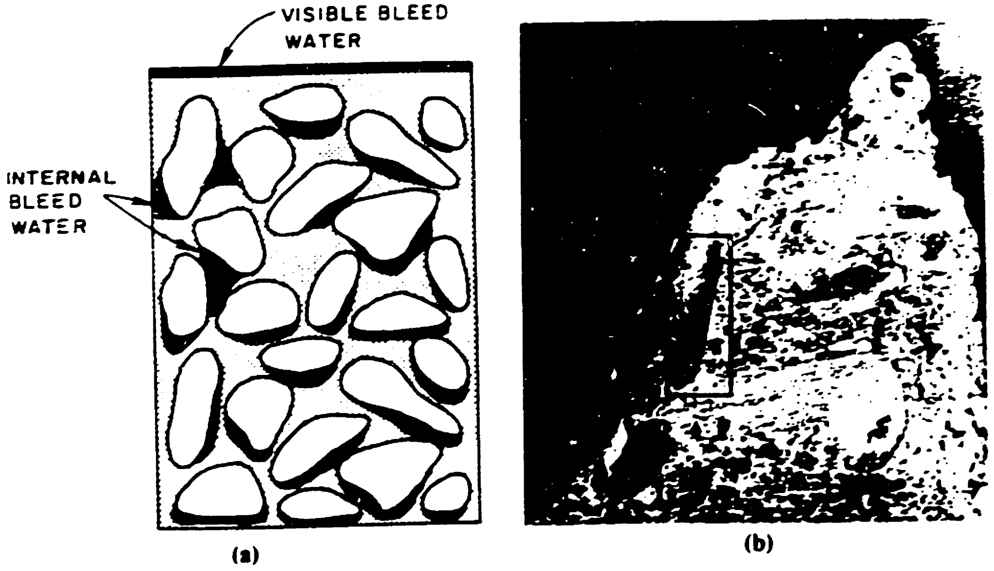
It is generally not considered detrimental to the concrete to have unhydrated cement grains other than the cement grains contribute less than C-S-H to the strength of the concrete. Unhydrated cement can in fact be advantageous because it allows for autogenuous healing of cracks. A certain amount of cracking is unavoidable in concrete, if there is unhydrated cement in the presence of moisture cracks may, to a certain extent, heal themselves by continued hydration. Hydration is a continuous process, although there may be a considerable amount of unhydrated cement in young pastes, in mature pastes it typically does not amount to more than 5% by volume. The exception is high strength concretes, these are formulated at such a low w/c ratio that there may be considerable amount of unhydrated cement.

5.2 Transition Zone

The transition zone is composed of same elements as the bulk paste but it has a different structure and different properties. Cement particles tend to pack less densely close to the coarse aggregate [Young, 1992], in addition, water films tend to form around large aggregate particles. Depending on aggregate size and grading there may be a considerable difference between the w/c ratios of the matrix and transition zone. In particular, there are likely to be areas of high w/c ratio under large aggregate particles due to internal bleeding of the concrete.

The strength of the paste depends on the volume and size of voids, both because the adhesion between hydration products and aggregates is due to van der Waals forces and because voids serve as stress concentrators. At early ages, the volume and size of voids in the transition zone will be larger than in the bulk matrix. This is in part due to the higher w/c ratio and thus higher initial porosity. In addition, crystals in the vicinity of the coarse aggregate are larger as a result of the higher w/c ratio and form a more porous framework. These voids, remnants of the space originally filled by mix water, are capillary pores, they are not considered part of the paste structure.

Another major factor responsible for the low strength of the transition zone is the presence of microcracks. The amount of microcracking in a particular concrete will depend the aggregate size and grading, cement content, w/c ratio, degree of consolidation, curing conditions and thermal history of the concrete. As the concrete



(a) Diagrammatic representation of bleeding in freshly deposited concrete; (b) shear-bond failure in a concrete specimen tested in uniaxial compression.

Internal bleed water tends to accumulate in the vicinity of elongated, flat, and large pieces of aggregate. In these locations, the aggregate-cement paste transition zone tends to be weak and easily prone to microcracking. This phenomenon is responsible for the shear-bond failure at the surface of the aggregate particle marked in the photograph.

Figure 5-3: Bleeding in Fresh Concrete [Mehta and Monteiro, 1993]

hydrates, the heat of hydration causes the temperature to rise. Subsequent cooling to ambient temperature results in differential movements between hydrated paste and aggregate and this in turn can cause tensile stresses and cracking.

These microcracks are also what is responsible for the low tensile strength of concrete.

It does not take very high energy levels to extend the cracks already existing in the transition zone, even at 40 % of ultimate strength, concrete may show plastic deformation and a decreased modulus of elasticity. At stresses greater than 70% of ultimate strength, stress concentrations at large voids in the the matrix can become large enough to initiate cracking. With increasing stress, these matrix cracks grow and join transition zone cracks; when the crack system becomes continuous the material ruptures. Considerable energy is needed for formation and extension of matrix cracks under a compressive load however cracks can propagate at a much lower stress level under tensile loading.

With increasing age the strength of the transition zone may become equal to or greater than the strength of the bulk matrix. This is due, in part, to the crystallization of new products from slow chemical reactions between the aggregate and calcium hydroxide the paste; siliceous aggregate will form calcium silicate hydrates, limestone will form carboaluminate hydrates. These new products increase the strength of the transition zone both because they reduce the volume of voids and because they reduce the concentration of calcium hydroxide. Since the large calcium hydroxide crystals have lower surface area than the same amount of C-S-H, the van der Waals forces are weaker, thus there is less adhesion. In addition, they can serve as preferred cleavage sites since they tend to form in oriented layers. The rate at which the strength of the transition zone increases, as well as its ultimate strengths, will depend on a number of factors, including the amount of microcracking and volume of voids.

5.3 Dimensional Stability

Each of the three major models (Feldman-Sereda, Powers-Brunauer, Munich) recognizes that water plays an important role in the behavior of C-S-H and thus of concrete. If unloaded concrete is kept at 100% relative humidity, it will be dimensionally stable indefinitely. At less than 100% relative humidity, however, it will tend to lose water and shrink. The water in concrete is typically classified according to its location within the paste structure. It can be either bulk water, capillary water, adsorbed water, interlayer water or hydroxyl water in the solid lattice. There appears to be neither a hard distinction between some of the forms of water however nor are there universally accepted methods for distinguishing between them.

Bulk water is water that is too far away from the surfaces of the paste solids to be under the influence of any attractive forces. Most of the water in capillary voids larger than 50 Åis bulk water. This is the first water lost on drying and since it is not attached to the paste by any chemical or physical bonds, there is no volume change. A saturated concrete can thus lose a considerable amount of water before there is any shrinkage.

Capillary water is that held by capillary tension, primarily in capillaries smaller than 50 Å. If it is removed, a compressive stress is induced in the walls of the pores thus causing contraction and shrinkage. After most of the free water has been lost, the concrete will start to lose capillary water and adsorbed water.

Adsorbed water is physically adsorbed on the surfaces of the hydration products. It is held by hydrogen bonding up to six molecular layers (15 Å) deep. The bond energy decreases with distance from the surface however and a major portion of the adsorbed water will be lost if the concrete is dried to 30% relative humidity. It is the loss of adsorbed water that is mainly responsible for the shrinkage of concrete during drying. Since adsorbed water is confined between the layers of the C-S-H, it tends to cause a disjoining pressure. When it is lost the disjoining pressure is reduced and the C-S-H shrinks.

In addition to the water adsorbed on the surface on the hydration products there is a monomolecular water layer within the layers of the C-S-H. Since this interlayer water is close to the C-S-H surface it is strongly held by hydrogen bonding. It is also somewhat trapped inside the C-S-H structure. As a result, it is only lost on strong drying (below 11% relative humidity). The C-S-H structure shrinks considerably when the interlayer water is lost.

The hydroxyl water in the crystal lattice is chemically combined and is thus an integral part of the hydrations products. This water is not lost until the hydrates decompose at high temperatures.

5.3.1 Drying Shrinkage vs. Creep

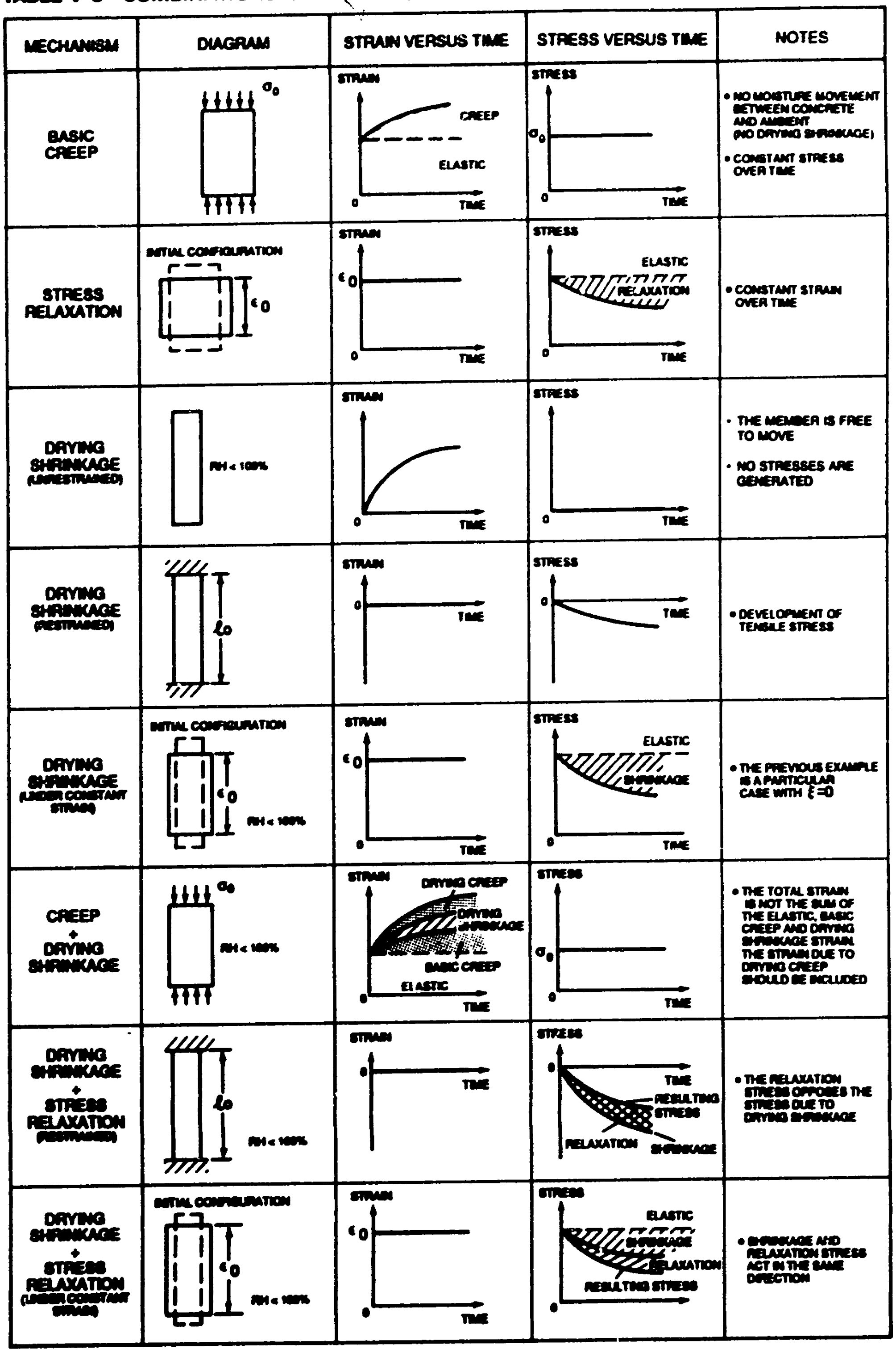
When concrete is subject to a constant stress under conditions of 100 % relative humidity there is an increase in strain over time referred to as basic creep. Similarly, exposing an unloaded, unrestrained concrete specimen to low relative humidity causes drying shrinkage which increases with time. In either case if the specimen is restrained (not free to move) there will be no strain but tensile stresses will develop.

Although the driving forces for drying shrinkage and creep are different, both are functions of the paste phase and both are primarily due to the loss of adsorbed water. With drying shrinkage, the driving force is a differential relative humidity between the concrete and the environment, with creep, the cause is sustained external stress. In addition to moisture movements, creep has other causes, in particular microcracks in the transition zone can be significant, nevertheless the loss of adsorbed water is considered to be the most important factor. A minor cause of both drying and creep shrinkage is the loss of water held by hydrostatic tension in small capillaries (< 50 nm) [Mehta and Monteiro, 1993].

In practice, drying shrinkage and creep usually take place simultaneously. However when concrete is under load and simultaneously exposed to low relative humidity, the total strain is usually more than the sum of the elastic strain, the free shrinkage strain (drying shrinkage of unloaded concrete) and basic creep without shrinkage. The additional creep that comes when the specimen under load is also drying is called drying creep and is thought to be caused by additional microcracking in the transition zone. Total creep is the sum of basic and drying creep, i.e. the deformation in excess of the elastic and drying shrinkage strains.

The strain-time curves for drying shrinkage and creep are similar and the factors that influence drying shrinkage generally influence creep in the same way. The microstrains of both are on the order of 400 to 1000 x 10^{-6} (400 to 1000 millionths), i.e. large enough so they usually cannot be ignored. The interaction between shrinkage and cracking is somewhat difficult to predict however because under continuous strain, tensile stresses are reduced due to stress relaxation. Both drying shrinkage and creep are reversible to some extent. The irreversible portions are assume to be the result of bond development within the C-S-H structure. Once pores collapse due to drying or creep, bonds can develop between the pore walls. These bonds may prevent the concrete from returning to its original dimension once it is rewetted or the load is removed. Figure 5-4 on the following page shows some of the relationships between drying shrinkage and creep.

TABLE 4–3 COMBINATIONS OF LOADING, RESTRAINING, AND HUMIDITY CONDITIONS



MECHANISM	DIAGRAM	STRAIN VERSUS TIME	STRESS VERSUS TIME	NOTES
BASIC CREEP	σ_0	STRAIN CREEP ELASTIC 0 TIME	STRESS σ_0 0 TIME	• NO MOISTURE MOVEMENT BETWEEN CONCRETE AND AMBIENT (NO DRYING SHRINKAGE) • CONSTANT STRESS OVER TIME
STRESS RELAXATION	INITIAL CONFIGURATION ϵ_0	STRAIN ϵ_0 0 TIME	STRESS ELASTIC RELAXATION 0 TIME	• CONSTANT STRAIN OVER TIME
DRYING SHRINKAGE (UNRESTRAINED)	RH < 100%	STRAIN 0 TIME	STRESS 0 TIME	• THE MEMBER IS FREE TO MOVE • NO STRESSES ARE GENERATED
DRYING SHRINKAGE (RESTRAINED)	ℓ_0	STRAIN 0 TIME	STRESS 0 TIME	• DEVELOPMENT OF TENSILE STRESS
DRYING SHRINKAGE (UNDER CONSTANT STRAIN)	INITIAL CONFIGURATION ϵ_0 RH < 100%	STRAIN ϵ_0 0 TIME	STRESS ELASTIC SHRINKAGE 0 TIME	• THE PREVIOUS EXAMPLE IS A PARTICULAR CASE WITH $\xi=0$
CREEP + DRYING SHRINKAGE	σ_0 RH < 100%	STRAIN DRYING CREEP DRYING SHRINKAGE BASIC CREEP ELASTIC 0 TIME	STRESS σ_0 0 TIME	• THE TOTAL STRAIN IS NOT THE SUM OF THE ELASTIC, BASIC CREEP AND DRYING SHRINKAGE STRAIN. THE STRAIN DUE TO DRYING CREEP SHOULD BE INCLUDED
DRYING SHRINKAGE + STRESS RELAXATION (RESTRAINED)	ℓ_0 RH < 100%	STRAIN 0 TIME	STRESS 0 TIME RESULTING STRESS RELAXATION SHRINKAGE	• THE RELAXATION STRESS OPPOSES THE STRESS DUE TO DRYING SHRINKAGE
DRYING SHRINKAGE + STRESS RELAXATION (UNDER CONSTANT STRAIN)	INITIAL CONFIGURATION ϵ_0 RH < 100%	STRAIN ϵ_0 0 TIME	STRESS ELASTIC SHRINKAGE RELAXATION RESULTING STRESS 0	• SHRINKAGE AND RELAXATION STRESS ACT IN THE SAME DIRECTION

Figure 5-4: Effects of Creep and Shrinkage [Mehta and Monteiro, 1993]

Chapter 6

Specialty Cements

As has been discussed in detail in previous chapters, there is a considerable difference between setting and strength development. The aluminates in cement are primarily responsible for the stiffening and setting behavior, the silicates are responsible for the long term strength development. Cements can be formulated to be rapid setting, have high early strength or both. To have high early strength, the hydration of the silicates must be accelerated, if just the aluminates are accelerated, the cement will achieve initial set faster than normal but strength development will then stop until the silicates begin to hydrate as usual.

Although Type III cement has higher early strength than Type I cement, it is not particularly rapid setting. Since its composition is essentially the same as Type I cement (with only a slightly higher C_3S and C_3A content), it sets at about the same rate. Its high early strength is primarily due to the fact that the cement is finer and thus more reactive. There have been a number of attempts to develop modified calcium silicate cements which have accelerated set times and further increase early strength development. Ultra High Early Strength cement, patented in England in 1973 (British Agreement Board Certificate No. 73/170), has a high C_3S content and a Blaine fineness of 700-900 m^2/kg (as opposed to Type I cement which is about 350 m^2/kg and Type III which is about 500 m^2/kg). It is made by separating the fines out from Type III cement with a cyclone air elutriator. Reportedly concrete with a strength of 12 MPa at 8 hr and 39 MPa at 24 hours was produced by using a high cement content (cement/aggregate ratio of 1:3) and a water/cement ratio of 0.4 [Mehta and Monteiro, 1993]. There is (or was) a cement sold in England known as extra-rapid-hardening cement which is a Type III cement with interground calcium chloride [Mindess and Young, 1981]. Grinding the calcium chloride increases its surface area and thus its reactivity however the overall performance may not be substantially different than if calcium chloride is added during mixing. A super-high-early-strength cement developed in Japan has a C_3S content exceeding 70% and traces of chromium, manganese and fluoride which reportedly increase the rate of hardening. It is not clear whether cement was ever commercially available. [Mindess and Young, 1981].

There is a limit to what can be accomplished by merely increasing the fineness and C_3S content of the cement however. In addition the very fine cements are both very difficult to work with and have a very high heat of hydration. There have thus been numerous attempts to formulate cements based on reactions that proceed more rapidly than the C_3S hydration.

A large number of rapid setting cements have been developed, particularly for highway applications. These include such products as Day Chem Perma Patch from Dayton Superior, Quickcrete from Quickcrete Systems, and Road Patch from Thoro Systems. Many of these cements are based on phosphate compounds including ammonium phosphate, silico phosphate and sodium hexametaphosphate. By and large however, these products are promoted as patching cements rather than cements with which one would make structural concrete, they tend to have very low tensile strengths even compared to Portland cements. Many of them are used primarily as mortars although the product literature may say that they can be extended with larger aggregate (typically on the order of 3/8"). Often the only type of mechanical testing done on these materials is compression testing and then on 2" mortar cubes. Long term durability performance has not been established for many of them and since they are manufactured in fairly small quantities they also tend to be extremely expensive compared to Portland cement.

Two specialty cements which have received considerable mention in the literature (including the previous extruded tunnel lining work) are regulated set cements and Very High Early cement (VHE). Both of these cements are formulated to develop a large amount of ettringite very quickly and they both develop considerable strength within 1 to 2 hours after casting. Although neither of these cements appear to be commercially available at this time, there are two similar cements which have been investigated in recent years for use in highway construction. Concretes made with these two cements, Rapid Set from CTS Systems and Pyrament from Lone Star Cement, were tested as part of a Strategic Highway Research Program (SHRP) project. Test data seemed to show these concretes had superior performance, in terms of strength development, to the highway department early strength mixes. They also tended to experience less of a rise in temperature which can be important with respect to thermal shrinkage and cracking.

Rapid setting cements are somewhat similar to expansive cements whose unique properties are also the result of ettringite formation. Rapid setting cements are formulated to produce the ettringite much faster than expansive cements however. Most of the ettringite forms before the calcium silicates have hydrated and the paste have developed a structure, thus it does not cause expansion.

The initial and final sets of rapid-setting cements (as measured by a Vicat test) typically occur very close together. As a result, rather than distinguishing between set times, it is customary to refer to a working time or handling time. This is typically the quantity of interest with respect to construction, it indicates how quickly the material must be placed. All of these products contain large amounts of alumina, thus resistance to sulfate attack is an important issue. In addition, ettringite adsorbs considerable water as it forms so care must be taken to make sure the concrete does not dry out during curing. The specifications for the proprietary cements typically recommend either wet curing or application of a curing compound.

Another cement based completely on the hydration of alumina is Calcium Aluminate Cement. Although it is not currently being used as a structural cement it has some very interesting properties and is worth review.

6.1 Regulated Set Cement

Regulated-set cement, also called reg-set, was developed by the Portland Cement Association in the late 1960's specifically as a rapid-setting, high early strength cement (U.S. Patents 3,628, 973 and 3,782,992). At one time, it was being produced by a number of cement companies (two mentioned in the literature are the General Portland Cement Company and the Huron Cement Company), the composition and thus the setting times and workability ranges varied slightly from company to company. It is not currently begin produced in North America however. The patent was acquired by the Onoda and Sumitomo Cement Companies of Japan, they combined this patent with some of their own patents and marketed the resulting product as "jet-set cement" [Uchikawa and Kiyoshi, 1983]. It is apparently still being produced in Japan [Mehta and Monteiro, 1993] and perhaps in Germany.

Reg-set cement is based on a modified Portland cement clinker containing C_3S and a calcium fluoraluminate, $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$. The cement can either be produced directly or the fluoroaluminate can be blended with a Type I clinker and $CaSO_4$ (anhydrite). The final cement in both cases typically contains 20-25 % fluoroaluminate and 10-15 % gypsum. $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$ is even more reactive than C_3A, it hydrates so rapidly that flash setting will occur unless a large amount of sulfate ions are present. The reaction with sulfate ions to form ettringite is also rapid. Hydrated gypsum does not dissolve fast enough to supply the sulfate; to avoid flash setting, anhydrite gypsum is used. Sodium sulfate and calcium sulfate hemihydrate (plaster of paris) are also used sometimes.

Even with sulfate present, the working time of the cement is generally very short (typically 3 - 5 minutes), however it can regulated fairly exactly up to about 40 minutes using organic retarders, citric acid has been found to be the most effective retarder. The high reactivity of the cement is confirmed by the high heat of hydration. Compared to Type I cement which has a heat of hydration of 80 to 90 cal/gram at 7 days and 90 to 100 cal/gram at 28 days, reg-set produces 100 to 110 cal/gram at 3 days.

Strength development occurs very rapidly after setting and strengths of 7 MPa (1000 psi) can be attained within 1 hour. This initial strength is due to ettringite forming from the $11CaO \cdot 7Al_2O_3 \cdot CaF_2$. Once this reaction slows down, strength development also slows down until the C_3S begins to hydrate as usual. The amount of early strength developed depends on the amount of fluoroaluminate used, this can be controlled by varying either the cement content of the concrete or the fluoroaluminate content of the cement. Strengths of more than 20 MPA (3000 psi) after 1 hour were achieved in laboratory testing using cements with 50% by weight of $11CaO \cdot 7Al_2O_3 \cdot CaF_2$ [Hewlett, 1988], the heat of hydration for such a mix is extremely high however. If the handling time of a mix is extended (i.e. with citric acid), it will take longer to reach a given strength.

Because of the high aluminate content, the sulfate resistance of the cement is low, most other concrete properties are similar to ordinary Portland cement however. A chemical analysis of Jet Set versus Portland cement is shown below (F is fluorine):

Chemical Analysis of Portland Cement versus Jet Set

Oxide	Portland Cement	Jet Set
SiO_2	21.3 %	14.5%
Al_2O_3	4.5	11.4
Fe_2O_3	4.0	1.5
MgO	2.4	.9
CaO	63.1	58.2
F	-	.9
Na_2O	0.1	.3
K_2O	1.2	.5
SO_3	2.2	10.3

The compound composition is given as:

C_3S	53.5 %
C_2S	1.1 %
$C_{11}A_7.CaF_2$	4.6 %
$CaSO_4$	16.3 %

6.2 Very High Early (VHE)

Regulated-set cement derives its rapid setting and hardening characteristics from the rapid formation of large amounts of ettringite. A cement with similar behavior called Very High Early Cement (VHE) was patented in 1975 by U.S. Gypsum (U.S. Patent 3,860,433). In VHE however, the source of the aluminate ions for the ettringite is $C_4A_3\bar{S}$ rather than calcium fluoroaluminate. This is the same compound used to produce ettringite in Type K expansive cements, but the quantity in VHE cement is greater.

Calcium sulfate is added to the initial raw mix in order to form $C_4A_3\bar{S}$ in the kiln. Calcium sulfate ($C\bar{S}$, soluble anhydrite) is used to control set, it is either formed in the kiln or added during grinding. The major calcium silicate compound is C_2S, VHE does not contain either C_3S or C_4AF.

Like reg-set cements, citric acid can be used to vary the setting time of VHE between 2 and 45 minutes. Initial strength development is similar to reg-set cements and strengths of 7 MPa (1000 psi) can be attained within 1 hour of set. Later strengths are higher than either reg-set cements or normal Portland cements, under normal curing (i.e. without steam) it can develop 15 MPa in 8 hours, 25 MPa in 24 hours, and 50 MPa ultimate strength. Although the initial formation of ettringite will be accompanied by a high heat of hydration, the subsequent hydration of C_2S does not cause a considerable temperature rise. In addition, since C_2S produces less calcium hydroxide than C_3S, it has good sulfate resistance. Creep and drying shrinkage are reportedly lower than for Type III cement concrete [Mindess and Young, 1981].

Foster-Miller (1983) did considerable testing with VHE cement concretes, including evaluating its behavior in their prototype slipform. They experienced problems with the slipform jamming which they attributed to the expansion of the concrete due to its rise in temperature. Normally Portland cement does not expand to any significant degree during hydration and certainly not enough to exert sufficient pressure to cause jamming of the slipform. As noted above however, the compound responsible for the high early strength of VHE cement is the same compound which creates the expansion in Type K expansive cement. If there was a problem with the formulation of the cement there may have been excessive expansion. Foster-Miller apparently did not pursue the matter.

6.3 Duracal

Duracal, another U.S. Gypsum product, is a combination of Type V cement and gypsum. Although it is fast setting, it is not completely durable under water, this makes it of questionable value for use in a tunnel. Although there is considerable mention of Duracal in the literature, it is not clear whether it is still being manufactured or in fact whether it was ever commercially available.

6.4 Expansive Cements

It is worthwhile to briefly examine the behavior of expansive cements given their similarity to some of the proprietary rapid set cements. Expansive cements are hydraulic cements which, unlike Portland cement, expand considerably as they hydrate. In particular, they expand after they have passed final set. Although large expansion in an unrestrained cement paste can cause cracking, if the expansion is properly restrained by either rebar or steel fibers, a compressive prestress will develop. Typically the magnitude of expansion is small and the prestress developed is on the order of 0.2 to 0.7 MPa (25 to 100 psi). This is usually enough to offset the tensile stress due to drying shrinkage; cements which generate this amount of prestress are known as shrinkage compensating. If the magnitude of expansion is large enough to produce prestress levels on the order of 7 MPa (1000 psi), the cement is called self-stressing and can be used for the production of chemically prestressed concrete elements. In practice, it is difficult to reliably generate and restrain this much expansion, shrinkage compensating cements have been used quite successfully however.

The expansive cements manufactured in the US, referred to as Type K cements are based on a sulfoaluminate clinker. Rather than containing C_3A as Portland cement does, the clinker contains considerable amounts of the sulfoaluminate $C_4A_3\bar{S}$ along with C_3S, C_2S and C_4AF. When the $C_4A_3\bar{S}$ hydrates it produces considerable amounts of ettringite; to achieve better control over the amount of expansion, the sulfoaluminate clinker is customarily blended with Type I or II clinker.

Two other expansive cements no longer commercially produced in the US are Type M and Type S expansive cements. They differ from Type K cement with in the source of the aluminate ions for the ettringite formation. Type M expansive cement is a mixture of Portland cement, calcium aluminate cement and calcium sulfate. Type S expansive cement is a very high C_3A cement (approximately 20 % C_3A) that has large amounts of calcium sulfate.

In general, ettringite-forming expansive cements are quick setting and prone to rapid slump loss. This is a consequence of the fact that ettringite forms rapidly and incorporates a considerable amount of water into the crystal. The stoichiometry for the reactions is shown below. The calcium hydroxide (CH) for the Type K and M reactions is provided by the hydration of the Portland clinker.

$$C_3A_3\bar{S} + 8C\bar{S} + 6CH + H_2O \rightarrow C_3A{\cdot}3C\bar{S}{\cdot}H_{32} \qquad \text{Type K}$$

$$CA + 3C\bar{S} + 2CH + H_2O \rightarrow C_3A{\cdot}3C\bar{S}{\cdot}H_{32} \qquad \text{Type M}$$

$$C_3A + 3C\bar{S} + H_2O \rightarrow C_3A{\cdot}3C\bar{S}{\cdot}H_{32} \qquad \text{Type S}$$

Type K clinker blended with Type II cement has excellent durability to sulfate attack because it contains very little reactive alumina or monosulfate after hydration. Type M and S clinkers however are not recommended for sulfate environments since they produce significant amounts of compounds that are vulnerable to sulfate attack.

6.5 Calcium Aluminate Cement

Calcium aluminate cement (CAC), also known as high alumina cement (HAC) was developed by Lafarge Calcium Aluminates as a high early strength, sulfate resisting cement. Unlike Portland and modified Portland cements in which C_3S and C_2S are the principal cementing compounds, the monocalcium aluminate, CA, is the principal cementing compound in CAC. CAC possesses many unique properties, it has high early strength, it hardens even at low-temperature and it has superior durability to sulfate attack. However it also tends to lose strength over time, this has caused several structural failures and consequently, CAC is no longer used for structural applications - in most countries it is now used mainly for making refractory linings for high temperature furnaces. CAC is typically about 60% monocalcium aluminate, 10% C_2S, 5 - 20% C_2AS and 10 - 17% various forms of iron. (Bauxite, a hydrated aluminum mineral is the most common source of the alumina and most bauxite ores contain considerable amounts of iron as an impurity.) Chemically, most CAC is about 40% Al_2O_3, some are as high as 50 to 80% Al_2O_3.

The unique properties of CAC are due to both the hydration characteristics of the cement and the microstructure of the hydrated paste. Although its setting time is similar to that of Portland cements, its early strength gain is very rapid due to the reactivity of the CA. After an initial dormant period CA hydrates quite rapidly and forms one of three calcium aluminate hydrates, depending on the temperature:

- at less than 10 °C, it forms CAH_{10}
- between 10 and 25 °C, it forms C_2AH_8 and aluminate hydrate (AH_3)
- at temperatures above 25 °C, it forms C_3AH_6 and aluminate hydrate

Within 24 hours of hydration, the strength of normally cured CAC can attain values exceeding the 7-day strength of ordinary Portland cement, about three-fourths of the ultimate strength is attained by this time. Since there is no calcium hydroxide (CH) in the hydration products, CAC concretes have excellent resistance to acidic environments (dilute acids 4 to 6 pH), seawater and sulfate waters. In addition they are stable at high temperatures (Portland cement concretes cannot be used above about 500 °C, the CH decomposes to free CaO which causes the concrete to become unsound).

The problem with CAC is that CAH_{10} and C_2AH_8 (the initial hydration products if the temperature is less than 25 °C) are thermodynamically unstable. If the temperature subsequently rises above 30 °C, these compounds convert to C_3AH_6 which is considerably denser (CAH_{10} has a density of 1.72 g/cm^3) whereas C_3AH_6 has a density of 2.52 g/cm^2). As a result of this conversion, the porosity of a hardened CAC paste can increase over 50%. Since this causes considerable disruption of the paste microstructure there can be a significant loss of strength.

The real concern with tunnel linings may not be that the residual strength will be inadequate but that as a result of the increase in porosity, there will also be a significant increase in permeability. In addition to possible problems due to leakage, this increases susceptibility to atmospheric carbonation and corrosion of any embedded steel. C_3AH_6 itself is also less resistant to sulfates and chlorides than CAH_{10} and C_2AH_8. Conversion is most rapid in a warm, humid environment and although it appears that temperatures have to be over 30 °C in order for the CAH_{10} to nucleate once it has nucleated, conversion will take place at 25 °C .

Given the superior properties of CAC there is considerable interest in finding applications in which it can used. It is marketed by Lafarge (under the tradename SewperCoat) as a mortar for lining and rehabilitating sewer pipes. In addition, there has been some research as far as use in the precast industry since it is fairly easy to control the curing environment in a precast plant. In the case of the CTBM however it will be impossible to completely control the curing environment, consequently the hydration products and behavior of the cement can not be guaranteed. It might

Figure 6-1: Conversion of Calcium Aluminate Cement

however be worthwhile pursuing how it would in fact behave in a tunnel lining and what it would take to be produce a lining with adequate strength and impermeability. Heat of hydration may be an addition concern however. The rate of heat liberation from a freshly hydrated CAC can be as high as 9 cal/g per hour which is three times as high as the rate for high-early-strength Portland cement. This may lead to considerable temperature differentials and cracking problems in the lining.

6.6 Pyrament Cement

Pyrament Cement (U.S. Patent 4,842.649) is one of the best known of the proprietary cements since it is quite heavily advertised. It has also has been fairly extensively tested both inhouse by its manufacturer (Lone Star Cement) and by independent testing laboratories. At this time however (January, 1995) Pyrament is no longer being manufactured. At some point Lone Star had filed for bankruptcy and as part of its restructuring plan it attempted to sell off several of its divisions. MasterBuilders, Inc. had contracted to buy the Pyrament division in November of 1994 but negotiations broke down over product liability and who would actually own the patent. Lone Star then decided to shut the division down. Cement production is a fairly expensive process in terms of the physical plant requirements so to be economically viable, it must be done large scale. Apparently Pyrament was not selling well enough to justify keeping the division open. (One of the reasons MasterBuilders was interested is that they have a very large sales force and they felt they would be able to increase sales.) Potentially it will be available again in the future, either from Lone Star or someone else.

Although the composition of Pyrament is held as trade secret, it is described as an alkali-activated aluminosilicate blended cement. There are three cements listed in the product catalog, they are all covered by the same patent number but are formulated to have slightly different setting times. PBC cement has a set time of 30-45 minutes, PBC-XT has a set time of 90-120 minutes and PBC-XXT has a set time of 160-220 minutes. The rate of strength development also varies. PBC is formulated to develop a strength of 2,500 psi (400 psi flexural) two and a half hours after mixing and a strength of 3,500 psi (600 psi flexural) after four and a half hours. PBC-XT is formulated to develop 2,500 psi (400 psi flexural) four hours after mixing (two hours after set) and 3,000 psi (600 psi flexural) six hours after mixing. PBC-XXT will develop 2,500 psi (400 flexural) approximately four hours after set (seven and a half hours after mixing). It will develop 3,000 psi (600 psi) approximately sixteen and one half hours after mixing.

A mix containing 752 lbs/cy (440 kg/m^3) of Pyrament per yard at a 3" slump is stated to develop the strengths shown on the next page.

PCB-XT Cement

Compressive Strength -	ASTM C 39, C 109	
4 hours	17.0 MPa	2,500 psi
1 day	34.0 MPa	5,000 psi
28 days	69.0 MPa	10,000 psi

Flexural Strength -	ASTM C 78	
4 hours	3.45 MPa	500 psi
28 days	8.27 MPa	1,200 psi

The product literature states that concrete made with Pyrament cement will typically have a cement content between 611 and 752 pounds per cubic yard and a w/c ratio between .25 and .29, presumably this is to get the strengths listed. According to their literature, a w/c ratio of .27 with 700 pounds of cement per yard will produce concrete with about a 5" slump. Strength results in the SHRP tests were considerably lower than what is given in the product literature however, a mix with 900 lb/yd^3 (530 kg/m^3) at a w/c ratio of .27 was cored and tested 6.2 hours after placing, it showed a strength of only 1650 psi. A mix with 850 lb/yd^3 (500 kg/m^3) and a w/c ratio of .29 was cored and tested 2.9 hours after placing, it showed a strength of only 1000 psi [Whiting, 1994].

On the basis of the ASTM test for sulfate resistance, ASTM C 1012, *Test Method for Length Change of Hydraulic Cement Mortars Exposed to Sulfate*, concrete made with Pyrament is highly sulfate resistant. The 120 day modulus of elasticity for PBC and PBC-XT is given as 5.2 x 10^6, however it is not clear whether this is a test value or a calculated value. No value is given for PBC-XXT although it is noted that PBC-XXT concretes exhibit a higher modulus than conventional concrete made with the same aggregates and having similar compressive strength, also that PBC-XXT's measured modulus of elasticity can be up to 20% higher than predicted using ACI 318 provisions. (The value given by ACI 318 tends to be low for most concretes however.) According to the Pyrament Contractor's Handbook, standard conveying methods can be used when placing the concrete but pumping will require more energy than conventional Portland cement concrete. This handbook also states that the concrete should not be wet cured (ponded), a membrane type curing compound is recommended. It stresses that neither admixtures nor Portland cement should be added to concrete made with Pyrament.

The product literature also lists a mortar (PBC cement and sand) referred to as Pyrament 505 Rapid Concrete Repair Material. Lab results for the 505 mix are shown on the next page, according to the product literature Pyrament 505 can be extended with up to 60% aggregate (30 pounds of aggregate per 50 pound bag). It is stated that when the mortar is extended 60 percent by weight with coarse aggregate, consistent with the depth of the repair area, strength reductions of 20 percent can be expected at early ages.

Lab Results for Pyrament 505 When Used as a Mortar

Compressive Strength - ASTM C 39, C 109

2 hours	17.0 MPa	2,500 psi
3 hours	24.0 MPa	3,500 psi
24 hours	41.0 MPa	6,000 psi
7 days	69.0 MPa	10,000 psi

Flexural Strength - ASTM C 78

3 hours	4.1 MPa	600 psi
1 day	6.9 MPa	1,000 psi
28 days	10.3 MPa	1,500 psi

6.7 Rapid Set Cement

Rapid Set Cement is manufactured by the CTS Cement Manufacturing Company. It is based on the same sulfoaluminate as VHE and Type K expansive cements. Like VHE it is formulated so that the ettringite is produced before the calcium silicates have hydrated, consequently it develops high early strength rather than expanding. CTS sells a number of admixtures including Rapid Set Set Control (a retarder) and Rapid Set Accelerator. It also sells a number of other cement products including an expansive cement and a non-shrink grout. The chemical formulation of Rapid Set versus a standard Portland Cement is shown on the next page.

Chemical Analysis of Portland Cement versus Rapid Set

Oxide	Portland Cement	Rapid Set
SiO_2	21.3 %	15%
Al_2O_3	4.5	14
Fe_2O_3	4.0	2
MgO	2.4	1
CaO	63.1	51
Na_2O	0.1	-
K_2O	1.2	-
SO_3	2.2	13

In the SHRP tests mentioned above, a mix with 750 pounds cement per cubic yard and a w/c ratio of .4 produced a core test strength of 3250 psi, 2.4 hours after placing. Citric acid was used as a retarder at the rate of 11.3 oz per yard. A mix with 550 pounds cement per cubic yard and a w/c ratio of .4 produced a core test strength of 3050 psi, 4.7 hours after testing. Citric acid was used as a retarder at the rate of 7.8 oz per yard [Whiting, 1994]. On the basis of these results, it appears that Rapid Set cement may have the potential to achieve the strengths required for the CTBM. It should be noted again however that strength development is not linear, i.e. you cannot really extrapolate four hour strengths from three hour strengths with any reliability.

The promotional literature for Rapid Set includes the following information about strength development for a concrete containing using 700 pounds of cement per cubic yard as well as strength development for their concrete mix (a pre-bagged mix of cement, sand and 3/8" stone). The literature states that a 60 pound bag of this mix yields about 1/2 cubic foot of concrete. It does not indicate how much cement is contained in a bag however. Both sets of tests are done on concrete with a five inch slump, there is no indication of what this is in terms of w/c ratio.

Strength Development of Rapid Set Cement and Concrete Mix

	Concrete with 700 lbs Cement/cubic yard	Concrete Mix
Compressive Strength -	ASTM C 39, C 109	
1 hour	2650 psi	2,000 psi
3 hours	3,700 psi	4,400 psi
24 hours	5,400 psi	5,500 psi
28 days	7,350 psi	7,500 psi
Flexural Strength -	ASTM C 78	
5 hours	650 psi	500 psi
1 day	700 psi	650 psi
28 days	1,200 psi	1,200 psi

Chapter 7

Concrete Aggregate

Because the aggregate used in concrete is relatively inexpensive and does not react chemically with water, there is a tendency to view it as simply an inert filler material. However since it makes up 60 to 75% of the concrete volume (70 by 85% of the weight) the aggregate can have a strong influence on the properties of both fresh and hardened concrete. The aggregate does in fact serve as an economical filler, however it also increases the dimensional stability and wear resistance of the concrete. Since the creep and shrinkage of concrete are due to changes in the paste fraction of concrete, minimizing the amount of paste in the concrete will minimize these volume changes.

As a general rule, aggregate should be hard, strong and free of undesirable impurities such as silt, clay and organic matter. Soft, porous rock or rock that tends to fracture easily along specific planes may limit strength and wear resistance, it may also break down during mixing and create an excessive amount of fine particles. Although deposits of coarse-grained soils, sometimes called bank gravel or bank run, are a good source of natural sand and gravel they usually contain varying quantities of silt and clay which must be removed by washing or dry screening. Silt and clay can coat the surfaces of the aggregate and interfere with the cement-aggregate bond, in addition they increase the water requirements of the concrete.

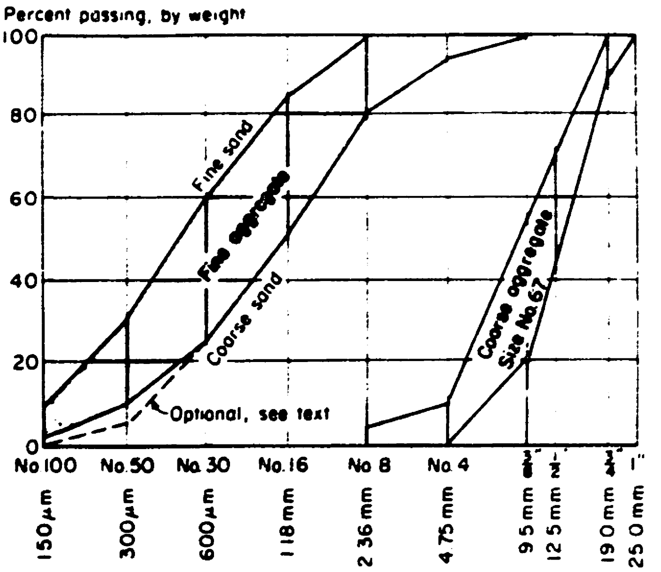
A knowledge of various aggregate characteristics (i.e. density, grading and moisture state) is required for proportioning concrete mixtures. Most natural mineral aggregate have a bulk density of 1520 to 1680 kg/m^3 (95 to 105 lb/ft^3) and produce concrete with a unit weight of approximately 2400 kg/m^3 (150 lb/ft^3). Bulk density is the weight of the aggregate fragments that fill a unit volume. Since it is impossible to pack aggregate fragments in such a way that there are no voids, the volume is made up of both aggregate and voids. The specific gravities of most natural aggregates are between 2.4 and 2.9 with corresponding mass densities of 2400 and 2900 kg/m^3 (150 and 181 lb/ft^3). Typical values for the specific gravities of granite, sandstone and dense limestone are 2.69, 2.65 and 2.60 respectively [Mindess and Young, 1981]. These are actually apparent specific gravities since they are the densities of the materials including internal pores. Typical porosities can be up to 2 % for intrusive igneous rocks, up to 5 % for dense sedimentary rocks and 10 to 18 % for very porous sandstones and limestones.

The unconfined compressive strength, abrasion resistance and elastic modulus of aggregate are a function of its porosity, and to a lesser extent, its mineralogic composition. Typical values of unconfined compressive strength for most granites, basalts, trap rocks, quartzitic sandstone and dense limestones are on the order of 210-310 MPa (30 to 45 ksi), typical values of dynamic elastic modulus are on the order of 70 to 90 GPa (10 to 13 x 10^6 psi) [Mindess and Young, 1981]. Given these values, the aggregate is typically not a limiting factor in the strength and elastic properties of concrete except with very high strength concretes.

7.1 Grading

The particle-size distribution (grading) of an aggregate can have a major impact on the amount of paste required for a workable concrete. Particle size distribution is determined through sieve analysis and usually expressed in terms of cumulative percentages passing or retained on a series of standard sieve sizes. Aggregate is typically divided into coarse and fine fractions, the coarse aggregate fraction is that larger then 4.75 mm (retained on the No. 4 sieve), the fine aggregate fraction is that smaller than 4.75 mm.

In the coarse aggregate range the sieves are referred to by the size of the openings,



Curves indicate the limits specified in ASTM C 33 for fine aggregate and for one typically used size number (grading size) of coarse aggregate.

Figure 7-1: Typical ASTM Grading Curves [Komatsu and Panarese, 1990]

in the fine aggregate range they are referred to by the number of openings per inch. Most sieve analyses are done with the standard sieve series given in ASTM C33, *Standard Specifications for Concrete Aggregates.* The sieve sizes for both coarse and fine aggregate are shown on the next page, as can be seen, each sieve is half the size of the next larger one (the No. 4 sieve has an opening size of 3/16 ").

ASTM Sieve Designation		Nominal Size	
		mm	in
Coarse Aggregate:	3 in.	75	3
	1 1/2	37.5	1.5
	3/4	19	.75
	3/8	9.5	.375
Fine Aggregate:	No. 4	.375	.187
	No. 8	2.36	.0937
	No. 16	1.18	.0469
	No. 30	600 um	.0234
	No. 50	300 um	.0124
	No. 100	150 um	.0059

7.2 Maximum Aggregate Size

The maximum size of the coarse aggregate influences both paste requirements and optimum grading for minimum voids. In general, the larger the maximum aggregate size, the smaller the surface area per unit mass or volume (specific surface) which has to be covered by paste. Using a larger maximum aggregate size can also reduce the void space. In normal strength concretes, strength increases with increasing aggregate size for a given workability and cement content. This is because less paste is required, therefore less water is required and the w/c ratio is lower. In high strength concrete the cement content may be such that increasing it further has little effect, the reduction in bond area and increased internal stresses that develop from larger aggregates actually tend to lower the strength.

The optimum maximum size of coarse aggregate for high-strength concrete depends on the relative strength of the cement paste, the cement bond and the strength of the aggregate particles. Due to both the variability and difficulty in determining these values the maximum aggregate size is often simply limited to 19 mm (3/4 in). It is not entirely clear if particle size would have a significant effect on early strength. The advantage in using smaller aggregate for high strength concrete is primarily due to the fact that the bond strength keeps increasing over time, using smaller aggregate means that there is more surface area for bonding, Although using smaller aggregate may also increase early strength, the increase is less significant and there are trade offs as far as the paste requirements.

In typical construction the maximum aggregate size is usually determined by job conditions. ACI 318 recommends that it not be greater than 1/5 the smallest dimension of the member or 3/4 of the minimum clear spacing between reinforcing bars or between the reinforcing bars and formwork. On most jobs this effectively limits the maximum size to 40 mm (1 1/2 in). In pumped concrete, the maximum aggregate size may be limited by the size of the lines.

For a given maximum aggregate size, a grading curve for minimum void space (and thus minimum paste requirements) can be worked out from particle geometries. The resulting distribution typically does not produce a workable concrete however. In order to have minimum voids some size gradations are left out, thus the concrete is prone to segregation. The objective in grading curves is to produce the minimum volume of voids that will not cause segregation, the grading for a given maximum size can be varied within a fairly large range without an appreciable effect on the paste requirements if there is sufficient fine aggregate to produce concrete of good workability.

ASTM C 33 includes thirteen specifications for coarse aggregate based on different maximum aggregate sizes. In order to allow for differences in the aggregate shape and texture, wide ranges are provided for each gradation. If an aggregate doesn't conform to the ASTM C33 grading limits, it doesn't mean it can't be used however, it just means that the concrete may require more paste and is more liable to segregate. In general, aggregates that do not have a large deficiency or excess of any size and give a smooth grading curve will produce the most satisfactory results.

7.3 Fine Aggregate Gradations

The fine aggregate gradations have the largest effect on workability. Variations in grading of the fine aggregate can seriously affect the uniformity of the concrete; large variations can cause unacceptable changes in workability. In practice, an empirical factor called the fineness module is often used to check the uniformity of the grading. The fineness modulus is computed by adding the cumulative percentages retained on each of the standard sieves and dividing the sum by 100, a higher fineness modulus indicates a coarser aggregate. An example of a fineness modulus calculation is shown below:

Fineness Modulus Calculation for Fine Aggregate

Sieve Size	% retained by weight	Cumulative % retained
3/8 "	0	0
No. 4	2	2
No. 8	13	15
No. 16	20	35
No. 30	20	55
No. 50	24	79
No. 100	18	97
Pan	3	-
	—	—
Total	100	283

Fineness Modulus = sum (cumulative percent retained) / 100= 283 / 100 = 2.83
Although the fineness modulus can be determined for coarse aggregate, it is usually only calculated for fine aggregate. It is actually a fairly crude measure of grading, two aggregates with the same fineness modulus can have quite different grading curves. Although it can be used to evaluate an aggregate and check grading when relatively

small changes are expected, it should not be used to compare the gradings of aggregate from different sources.

ASTM C33 recommends that the fine aggregate have a fineness modulus between 2.3 and 3.1 since very fine sands have high paste requirements and very coarse sands produce mixtures which are harsh and unworkable,. It also sets minimum requirements for the material passing the No. 50 and No. 100 sieves to ensure there is enough fine material to produce good cohesiveness and plasticity. The minima do not apply however if the concrete contains more than 500 pounds of cement per cubic yard or when mineral admixtures are used however; in these cases, the cement and/or admixture will contribute enough fine material. The very fine fraction (particles passing the No. 200 sieve) are limited to not more than 5% since such material has a very high water demand, in natural aggregate it is also likely to be rich in clay matter which can undergo large volume changes with changes in moisture. At this range the aggregate also overlaps the size of the cement particles, the very small aggregate effectively become part of the cement paste and reduces its adhesive capacities. Very small aggregate does however increase the amount of paste and thus will increase workability. There is no firm boundary between particles which should be considered part of the cement paste and particles which should be considered as aggregate.

The ASTM C33 grading specifications have only one specification for fine aggregate, it is shown on the next page. To ensure adequate workability, the fine aggregate should be 35 to 45 % by weight of the total aggregate. The amount of voids, water, cement and fine aggregate (i.e. the mortar fraction) should be 45 to 60 % by weight (50 to 65% by volume) of the concrete. When rounded coarse aggregate (gravels) are used, slightly less mortar is required.

ASTM C33 Grading Specifications for Fine Aggregate:

Sieve Size	% passing
3/8 "	100
No. 4	95 to 100
No. 8	80 to 100
No. 16	50 to 85
No. 30	25 to 60
No. 50	10 to 30
No. 100	2 to 10

7.4 Shape and Texture

The amount of paste required to produce a concrete of given workability will be a function of the aggregate shape and texture as well as its gradation. There needs to be enough paste to coat each of the aggregate particles and lubricate them so that the mix flows easily. Aggregate with a high specific surface will require more paste to coat its surfaces and rough surfaces require more paste for adequate lubrication.

The ideal particle, in terms of minimizing the amount of paste, is one that is well rounded and spherical in shape with a relatively smooth surface. Although most natural sands and gravel come fairly close to this ideal crushed stone is typically angular with sharp edges and corners and a rough surface texture. Such particles interfere with the movement of adjacent particles during mixing and handling. They also have a high surface to volume ratio. The shape and texture of the fine aggregate in particular can have a significant effect on mix proportions. Angular sands will require more paste for a given consistency, alternatively, they produce harsh and unworkable mixtures at a paste content that might have been adequate with a well-rounded sand.

Although the shape and surface texture of aggregate particles influence the properties of the fresh mix more than the hardened concrete the characteristics of the coarse aggregate will affect the aggregate-paste bond and thus the strength of the concrete. The requirements for minimum paste do not match the requirements for maximum strength however. If the objective is to maximize strength, aggregate which increases the amount of surface area and bonding should be used. Angular, irregular shapes with rough, coarse surface texture have greater surface area for bonding and better mechanical interlock between the aggregate particle in hardened concrete. Such aggregate offers higher potential compressive and tensile strength; for very high strength concretes, it is considered essential to use crushed rock as aggregate.

Extremes in aggregate shape may lead to high internal stress concentrations however, hence they are more prone to bond failure. Most specifications recommend that flat or elongated aggregated particles not be used; concrete containing aggregate of this shape is more prone to segregation as a result of the increased particle interaction and the high paste requirements. An excess of flat or elongated particles in crushed rock may also indicate the rock has weak fracture planes. Laminated limestones, sandstones and shale tend to produce elongated and flaky fragments.

By and large the effects of shape are more significant than the effects of surface texture. However it appears that strength at early ages, particularly flexural strength, can be affected by the aggregate texture - a rougher texture seems to result in a stronger physical bond between the paste and the aggregate. At later ages when the chemical bond between the paste and aggregate is stronger this effect is not as important [Mehta and Monteiro, 1993].

7.5 Aggregate Moisture

As noted above the aggregate particles all contain some degree of porosity. Water can be absorbed into the particle, there can also be a water film on the surface of the particle. As a result, the moisture content of a stockpiled aggregate can vary considerably. Aggregate is usually considered to be in one of four moisture states:

- 1. Oven dry (OD): all moisture is removed from the aggregate by heating it in an oven at 100 C until it reached constant weight, All pores are empty.

- 2. Air-dry (AD): there is no moisture on the surface and the internal pores are only partially full.
- 3. Saturate-surface-dry (SSD): all of the pores are filled, but there is no water on the surface.
- 4. Wet: all pores are completely filled with water and there is a film of water on the surface. The amount of water in excess of that required for the SSD condition is referred to as the surface moisture.

Absorption capacity is defined as the amount of moisture required to bring an aggregate from an oven-dry to a SSD condition. (The absorption capacity of an aggregate is easily determined and as a first approximation can be used as a measure of porosity and strength). Effective absorption is defined as the amount of moisture required to bring an aggregate from the air-dry to the SSD condition. Absorption values will be a function of the porosity of the rock; typical effective absorption values for trap rock, porous sandstone and expanded shale aggregate are 1/2, 5 and 10 percent respectively [Mindess and Young, 1981]. Values for the absorption capacity, effective absorption and surface moisture are needed for correcting the batch water and aggregate proportions. If there is a tendency for the aggregate to absorb water, it will be removed from the paste, thus lowering the w/c ratio and [illegible] the workability of the concrete. Conversely, if there is excess water on the aggregate surfaces, extra water will be added to the paste and the w/c ratio of the concrete will be higher than desired.

Stockpiled coarse aggregate is generally in an air dry state with an effective absorption of less than 1%. Fine aggregate on the other hand is often in a wet state with a surface moisture of up to to 5%. The reason for these high surface-moisture values is that menisci tend to form between particles. Thus in addition to the thin surface films, additional water can be held in the spaces between the particles.

Chapter 8

Fresh Concrete

8.1 Workability of Fresh Concrete

Concrete is typically considered to be in either a fresh or hardened state. There is neither a sudden change in properties nor any other specific indicator when concrete ceases to be fresh however; whatever parameters are used to distinguish between fresh and hardened concrete are therefore mostly arbitrary. Fresh concrete refers generally to the concrete during the time it is being mixed, placed and cured. With most concretes, the properties of the concrete in its hardened state, in particular its strength, are the most important. The properties of the concrete in its "fresh" state are only considered important in so far as they must make it possible to achieve the necessary ultimate strength. In the case of the CTBM however, the behavior of the fresh concrete is central to the overall performance of the machine. Consequently, its properties become important.

One of the problems in evaluating fresh concrete is that there is disagreement over what properties should be evaluated, what tests measure these properties and what terminology should be used. The most common terms used in describing fresh concrete is workability, according to ASTM C 125, *Definition of Terms Relating to Concrete and Concrete Aggregates*, workability is the property which determines the effort required to manipulate a fresh concrete with a minimum loss of homogeneity.

In other words, it is the property that determines how easily a concrete mixture can be placed, compacted and finished. It is not a quantitative measure however, in addition there is no standard requirement for workability, it depends on the type of construction and the equipment used to transport and consolidate the concrete - the workability required for pumped concrete is not the same as for concrete placed with buckets.

The amount of work required to place and compact concrete is largely determined by the amount of work needed to initiate and maintain flow of the mix. This is a function of the rheological properties of the cement paste, the internal friction between the aggregate particles and the external friction between the concrete and the formwork. Workability can be controlled by varying the water content, the cement content, the aggregate grading or using admixtures. It is actually a composite property however, it is a measure of both the consistency (fluidity) and the stability (cohesiveness) of the mix. The stability of a mix reflects its water holding capacity (resistance to bleeding) and its coarse-aggregate holding capacity (resistance to segregation). A change in mix design may influence the consistency and cohesiveness in opposite ways, as an example, when the amount of water is increased, the consistency (slump) will increase but the cohesiveness (stability) will decrease.

In general, the behavior of a concrete mixture is fairly predictable: concretes with very high consistencies have low stability, i.e. they tend to segregate and bleed, concretes with very low consistencies on the other hand are difficult to place and compact. Lowering the cement content considerably at a given water content tends to produce a very weak paste which results in a "harsh" mix i.e. one where there is considerable friction between the aggregate particles. Increasing the cement content considerably at a given water content or using a finer cement produces a paste which is very cohesive (sticky) and difficult to move.

The grading of the aggregate determines the amount of cement paste which is necessary to coat all of the particles and fill the interstitial spaces between them. The greater the proportion of fine particles, the greater the surface area of the aggregate and the quantity of cement paste necessary to coat the particles with a sufficiently thick layer. An excessively high content of coarse aggregate however will make the mix harsh and there may be voids between the coarse aggregate particles that are not filled with mortar. This will lead to a weaker and less durable hardened concrete. Aggregate which has a high proportion of flat, elongated or needle-like particles has poor compactability and low mobility because of the increased interactions between particles. This makes it difficult to remove trapped air and achieve the degree of consolidation required to obtain adequate compressive strength and durability.

8.2 Stability

The transport and placing of fresh concrete requires the mix to flow easily with a minimum of external effort and reach its final location without any significant changes in composition or properties. Stability is sometimes defined as the capacity of the fresh mix to maintain its initial uniformity during the process of transport, handling and placing, it can also be defined as the ability of the mix to resist bleeding and segregation. Although these two phenomena are related, bleeding typically refers to the loss of water from the mix, segregation is normally associated with a loss of uniformity in the distribution of the coarse aggregate.

Water is the lightest constituent in concrete, thus bleeding is a problem when the concrete is under pressure as in pumping since the water is more mobile than aggregate. Bleeding also occurs after the concrete is placed. Walls and columns in large structures are typically constructed via multiple layers or "lifts", bleeding will cause a weak interface between lifts; excessive bleeding in floors and slabs causes a weak surface and poor finish. Internal bleeding can have a negative impact on the structure of the concrete; water rising through the concrete gets trapped under rebar or pieces of large aggregate, this produces a transition zone with a locally high w/c ratio that is susceptible to microcracking.

Segregation is due to the fact that the large aggregate is heavier than the paste. No concrete mix is entirely resistant to segregation when subjected to incorrect handling, however, there is an increase risk of segregation when:

- - the concrete has a gap-graded aggregate (there is not a continuous range of particle sizes)

- - there is an inadequate proportion of fine aggregate - depending on gradation the fine aggregate should ordinarily be 30-40
- - there is inadequate content of cement paste, especially when combined with a lack of fine aggregate
- - there is an excessive proportion of angular, crushed-rock coarse aggregate
- - too high a w/c ratio - this reduces the viscosity of the cement paste, it is no longer cohesive enough to maintain a uniform distribution of the aggregate particles throughout the mix
- - too low a w/c ratio, the paste no longer behaves as a fluid, it is too dry to form a matrix and ceases to adhere to the aggregate particles, thus it cannot maintain the uniformity of the mix during handling.
- - the coarse aggregate is of a significantly different density than the fine aggregate (i.e. a mix where a light weight coarse aggregate is used with a normal weight sand)
- - there is an overdose of superplasticizer

The most common causes of segregation are impact, vibration of highly workable mixes and pumping. To minimize segregation on impact, fresh concrete should not be allowed to drop from excessive heights, free-fall drops of greater than 1.5 meters should be avoided.

8.3 Evaluating Fresh Concrete

Unlike hardened concrete where compressive strength is typically used as the criterion for evaluating quality, there is no single test for evaluating fresh concrete. Since concrete became a major construction material at the end of the 19th century a large number of tests have been developed to evaluate different properties of fresh concrete.

The results of some of these tests can be correlated with or converted to results from other tests but the scope of such conversion is often limited; some tests produce results which cannot be compared with any other tests. Recently attempts have been made to analyze some of these tests and establish theoretical models which simulate the procedures involved. There have also been attempts to explain and predict their results in terms of fundamental rheological characteristics. To date however there has been limited success [Bartos, 1992].

The slump test (ASTM C 143) is the most common field test. In theory, this test measures the consistency or flowability of the concrete. In actuality, it is most useful as a means of controlling batch to batch variations of a particular mix. i.e., a more than normal variation in slump may indicate that there is a problem with proportioning; there is no correlation between the results of the slump test and the rheological properties of the mix. Most mix design procedures rely on slump as a crude index of workability however since it does measure the consistency, at least in relative terms, and it does indicate how easily the mix will flow. It is assumed that mixtures containing adequate cement and well graded aggregates will have a satisfactory degree of cohesiveness. Of equal (if not greater) importance, the slump test can be easily carried out on a construction site.

On very stiff mixes and mixes containing fibers, the Vebe test may be used instead of the slump test. Two other tests, the Flow/Spread Table and the Compaction Factor test are sometimes used in Europe and Great Britain. Although the slump test is the only one covered by an ASTM standard, there are standards in Europe for the other tests. The Vebe and Compaction Factor tests are described in the British Standards (BS 1881: Part 2), the Flow/Spread Table is described in the German DIN 1048, Part 1. It should be noted that all four of these tests are strictly empirical, their results are not related to the rheological properties of the material

8.3.1 Slump Test

The slump test was developed in the U.S. around 1910, although specifications in different countries may differ slightly, it is now used world wide. In general, the test measures how much a sample of concrete, cast in the shape of a truncated cone, decreases in height after the cone is removed. The cone typically is 300 mm high and has a diameter of 100 mm at the top and 200 mm at the bottom. In order to maintain some degree of standardization in the results, there are specific procedures for filling and removing the cone. After the cone is removed, the difference in height between the cone and concrete is measured, in addition the type of slump is determined i.e true, collapsed, shear or zero/no-slump.

- True slump: the sample of concrete settles but it retains a symmetrical shape. There is a measurable difference between the height of the slump cone and the height of the slumped sample of fresh concrete. Tapping the sample with the tamping rod after determining the slump value can give an indication of the stability of the mix. The mix is stable if the tapping causes the slumped concrete to retain its shape and simply slump further. The mix is unstable and susceptible to segregation if the tapping causes the sample to shear or fall apart.
- No slump: after the removal of the cone there is no measurable difference between the height of the cone and the height of the concrete sample
- Collapsed slump: the slumped sample spreads out on the base and loses all trace of its original shape. In the case of a collapsed slump, the amount of slump is typically not recorded. Concrete which has slumped more than 200 mm (8 inches) is usually considered to have a collapsed slump.
- Shear slump: part of the sample shears off and collapses, the remaining part retains the slump shaped. Shear slump indicates a non-cohesive mix which may be unsuitable for assessment by the slump test, in most cases it indicates a mix with poor stability.

8.3.2 Vebe Test

The Vebe test was developed in Sweden in the 1920s by Victor Bahrner. It measures the time required to remould a sample of concrete cast in the shape of the slump test cone into a cylinder. During the remoulding, the concrete is subject to both vibration and pressure. The Vebe test is applicable to stiff, dry mixes which show very low (less than 20 mm) or zero slump. It is the most widely used test in the production of precast and prestressed concrete products where high strength, low workability concrete mixes are used. In particular it is appropriate for mixes which are compacted by intensive vibration, possibly combined with pressure. It has also been found to be more useful than the slump test in comparing steel fiber reinforced concretes.

The first stage of the test follows the procedure for the slump test and is carried out inside a cylindrical container. The slump cone is filled and removed according to the procedures of the slump test, a clear plastic disc is then placed on top of the concrete and the sample is vibrated. As the disc moves down, the contact area between the disc and concrete is observed. Once the underside of the disc is entirely in contact with concrete, the vibration is stopped. This time is measured to the nearest second and recorded as the Vebe time.

The workability of concrete suitable for the Vebe test is normally very low, hence the concrete can contain a considerable amount of trapped air which is expelled during the test. To allow for the change of volume, Bahrner suggested a correction factor. Since this tends to complicate the procedure without really providing more information, it was not adopted in practice.

The Vebe test is assumed to reflect the amount of energy required to remould and compact a constant quantity of concrete by vibration. It is sometimes difficult to judge the exact moment when the bottom of the disc becomes covered completely by paste however. This is particularly true when mixes with large aggregate and very low workability are tested. In such cases the largest stones can protrude from the surface and prevent the disc from completely contacting the cement paste.

8.3.3 Flow/SpreadTest Table

This test was developed in Germany in the 1930s, it is based on a sample of fresh concrete which has been moulded in the shape of a truncated cone and allowed to

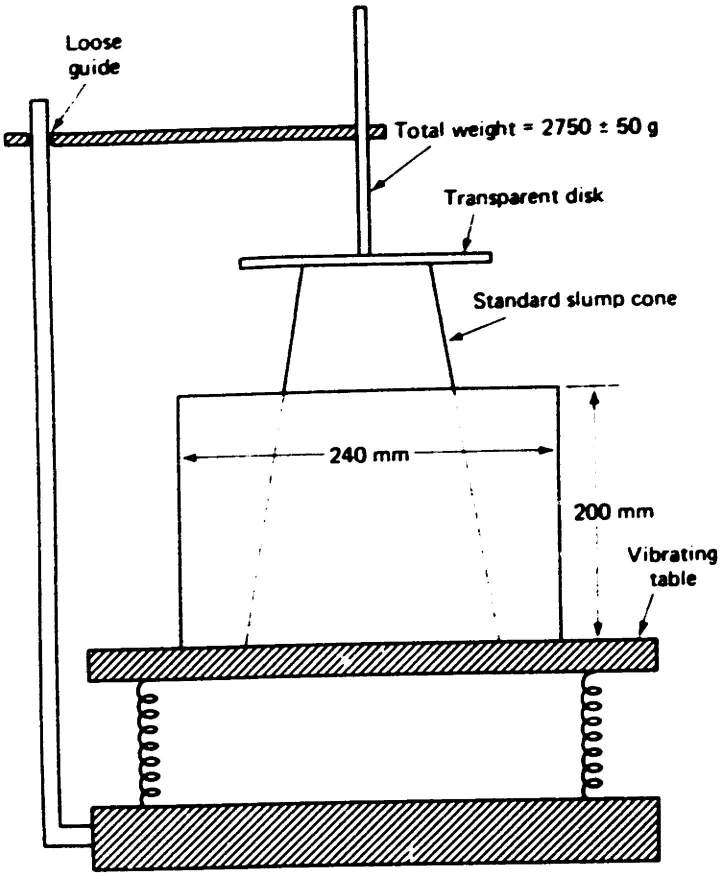


Figure 8-1: Vebe Test Apparatus[Mindess and Young. 1981]

slump. The slumped concrete is then subjected to a controlled amount of jolting and the amount it spreads is recorded. The test can be used for mixes very high workability where collapsed slumps are recorded, as a result it is useful for evaluating superplasticized and other special flowing fresh mixes. The test also gives an indication of the stability of the mix, unstable mixes prone to segregation and bleeding are indicated by a rim of water or paste surrounding the spread concrete at the end of the test.

The test apparatus consists of a flat, square top plate which has center lines engraved on it. The top plate is attached to a bottom plate by hinges along one side. these hinges allow the opposite side of the plate to be raised to a height of 40 mm. In the middle of the top plate, at the intersection of the two centerlines there is a 200 mm circle engraved. A cone is placed on the lines of this circle, filled with concrete and then removed. After the top plate is lifted and dropped 15 times at the rate of approximately one drop per second, the distance the concrete has spread along the two centerlines is measured.

There are a number of sources of possible error in this test: there could be excessive compaction of the concrete as the cone is filled, the cone could be positioned outside the circle marking the center, the plates could be warped or measurements could be incorrect. The main disadvantage of this test however is that it really does not simulate the placing of fresh concrete. In particular, jolting a fresh mix can lead to segregation in construction, as a result, such handling is normally avoid.

8.3.4 Compaction Factor Test

The Compaction Factor test was developed in Great Britain in the late 40s. Its objective is to measure the degree of compaction caused by the application of a standard amount of work to a sample of fresh concrete. It compares concrete which is partially compacted through the force of falling through a sequence of hoppers to concrete which has been fully compacted mechanically. It is appropriate for mixes with approximately the same range of workability as the slump test.

The basic test apparatus consists of a heavy duty stand with a base and a column. The column supports two funnel-shaped hoppers mounted one above the other; there is a cylindrical bucket beneath the lower hopper. At the start of the test, the upper hopper is filled with fresh concrete. The gate of the hopper is then opened, allowing the concrete to fall into the lower hopper. After all of the concrete has fallen into the lower hopper, the gate of this hopper is opened, allowing the concrete to fall into the cylinder. The concrete in the cylinder is then leveled off and the cylinder is weighed. This concrete is referred to as the "partially compacted" sample.

The cylinder is then emptied and re-filled with the same concrete which is compacted (either by rodding or vibrating) in order to produce maximum compaction. The cylinder is then weighed again. The compaction factor (CF) is the ratio of the weight of the partially compacted concrete to the fully compacted concrete

$$\text{CF} = \text{weight partial} \,/\, \text{weight full}$$

Although the compaction factor is related to the compactability of the fresh concrete, the manner in which the partial compaction is achieved and the amount of energy used during the test differs considerably from the normal concrete construction practice, normally compaction is done by vibration. Furthermore, in dropping the concrete through the hopper, not all the work is spent on compaction, a proportion of the constant work is lost due to friction between the concrete sample and the walls of the hoppers. Higher friction is likely to develop when stiff, dry, low workability concrete is tested. It is difficult to assess the loss of work through friction and in general, it cannot be said concretes showing the same Compaction Factor test results will in practice require the same amount of work for compaction.

The test results indicate approximately the following workabilities:

<.75 very low workability (suitability of the CF test is limited)
.75 - .85 low workability
.85 - .92 medium workability
.92 - .95 high workability
> .95 very high workability

The Compaction Factor thus provides some idea of the compactability of a fresh mix, an approximate correlation can be made between the slump test and the Compaction Factor. The variability of the CF test results increases with concretes of very low apparent workability however. This is thought to the due to the increased role and unpredictable nature of friction during the test. The Compaction Factor test is also oversensitive to composition, namely the water content of very high workability mixes. These mixes typically require very little work for full compaction, often much less than the amount which is provided during the Compaction Factor test. This test is actually not used very much (if at all) in the U.S., Great Britain is the only country which has a standard for it.

8.4 Mixing and Placing

Most specifications for concrete construction require batching by weight rather than volume because bulking of the fine aggregate can cause wide variations in quantities.

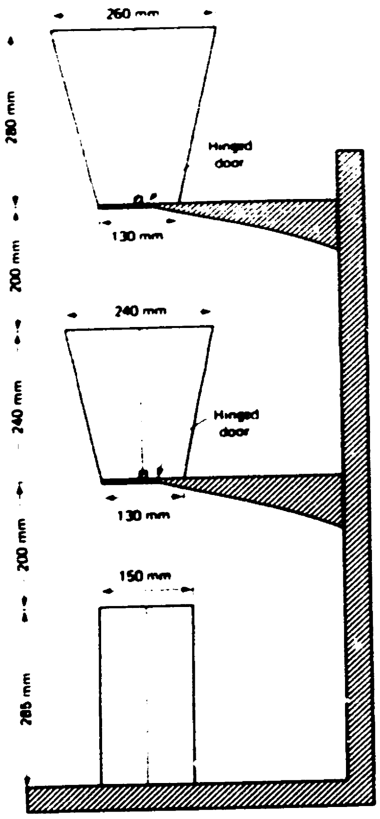


Figure 8-2: Compacting Factor Apparatus [Mindess and Young 1981]

Bulking occurs when the fine aggregate gets wet enough that menisci form between the particles. The menisci allow thick water films to form, these push the particles apart and increase the apparent volume of the aggregate. Coarse aggregate shows much less bulking than fine aggregate, since the particle size is large compared to the thickness of the water films the effect of menisci formation is slight.

In the case of the CTBM it is likely that a continuous (rather than a batch mixer) will be used. In continuous mixers the materials are fed into a mixing drum by means of special conveyor belts and the concrete is mixed as it passes through the drum to the discharge end. Since the materials are proportioned by adjusting the relative speeds of the conveyor belts, proportioning is actually by volume. In order to produce uniform concrete, it is important that the aggregate gradation is constant and the fine aggregate is at a constant moisture content (preferably dry). The conveyors also need to be well maintained in order to ensure an accurate supply of materials.

8.4.1 Preblending

Foster-Miller (1973) were using a mix that included fly ash to make up for a deficiency in the fine fraction of their sand. They experimented with preblending the aggregate (both coarse and fine), the fly ash and a portion of the mix water with the idea that only the cement, admixtures and remaining mix water would need to be added at the heading. They had a number of problems including segregation of the coarse aggregate and possible problems due to contamination of the blended materials with cement. These batches also produced concrete with a lower ultimate strength than previous tests; they proposed several possible explanations, one was that the aggregate became coated with fly ash and this reduced the aggregate-paste bond. Alternatively they thought it might have been due to compositional changes in either the cement or the fly ash. They did not pursue the matter further however. They also had other problems because the cement they were using (a Very High Early Cement) behaved erratically when contaminated with portland cement. In general preblending of two or more of the materials would appear to be a very good idea. This would simplify the operation at the tunnel face, both in terms of the storage space required and the procedures involved. It might take considerable testing however to determine which materials should be preblended, since this will be heavily dependent on the actual materials used, it might be different from project to project, depending on the mix design.

8.4.2 Mixing Time

With a typical truck mixer, optimum mixing time depends on a variety of factors including:

1.) the consistency of the mix
2). the condition of the mixer
3). the speed of rotation
4.) the size of the charge
5.) the properties of the constituent materials

Low slump mixes may require considerably longer mixing times and concretes made with angular aggregate need more mixing than those made with rounded gravels. A rule of thumb however is 1 minute of mixing time for 1 m^3 of concrete plus 1/4 minute for each additional 1 m^3 [Mindess and Young, 1981]. With a continuous mixer, the amount of mixing time will be function of how fast the concrete is conveyed through the mixing drum. Presumably the manufacturer would supply recommended speeds for various mixtures, nevertheless the actual mixing time should be determined by testing the materials which will be used.

8.4.3 Batching

The operation of adding materials to the mix is referred to as "batching" or "charging". Presumably the manufacturer of the continuous mixer will also supply recommendations on how to batch the materials since this will probably be different than for a truck mixer. Although batching operations for truck mixers vary, it is common to add about 10% of the mixing water before any aggregate is added. The water is then added uniformly the whole time the solid ingredients are added, leaving about 10% to be added at the end. The cement is batched after about 10% of the aggregate has been added, and in such a way that it is not directly hit by the mix water stream. Direct contact between the water and the cement tends to result in clumping or balling of the cement. These clumps, which have the consistency of modeling clay, can be very difficult to break up. Mineral admixtures are generally added with the cement but chemical admixture should be added with the mixing water. If more than one chemical admixture is used, they should be added separately in order to minimize interactions and allow one admixture to interact with the solid ingredients before the next is added. They should also be added in the same order each time.

8.5 Vibration and Compaction

After placement, concrete is typically vibrated to consolidate it and make sure the forms have been completely filled. Vibration eliminates voids and entrapped air which are (typically large) air bubbles that get caught in the concrete as it falls into the forms. The workability of most mixes, in particular their compactability is normally not high enough to allow this air to rise to the surface and dissipate without aid. Vibration also reduces the internal friction between the coarse aggregate particles; this allows the mix to flow more easily, particularly around rebar and other embedded items. Due to the reduction in air content, vibration usually increases the density of the concrete.

Internal, immersion vibrators (referred to as spud or poker vibrators) are the most common type. They consist of a cylindrical vibrating head, 20 to180 mm in diameter on a flexible shaft about 2 meters long. An eccentric rotating mass inside the head causes it to revolve in a circular orbit. The small (20mm) vibrators have frequencies ranging from 10,000 to 15,000 vibrations per minute and vibration amplitudes between .4 and .8 mm. [Mehta and Monteiro, 1993]. Vibrators with larger diameters have lower frequencies and higher amplitudes. External vibrators clamped to the formwork are typically used only when internal vibration is not practical (i.e. in sections which are very heavily reinforced or very thin). External vibrators require more power since they also impart energy to the formwork and are generally less effective than internal vibrators. Furthermore, the forms must be fairly strong and rigid, they should also remain watertight. External vibrators are generally run at between 2000 and 6000 rev/min.

Vibration causes sinusoidal compression waves to pass through the concrete, these compression waves subsequently generate oscillatory shear stresses. The response of the concrete will depend on its workability as well as the frequency and amplitude of the vibration, in general however, the shear stresses break the flocculated cement paste down and temporarily turn it from a Bingham fluid into a Newtonian fluid of lower viscosity. Vibration also sets the particles in motion; these effects combine to increase the the workability of the concrete enough so that the entrapped air is released and the particles of aggregate rearrange themselves into a denser packing under the effects of self-weight.

8.5.1 Internal Vibration

When internal vibrators are used, the energy imparted by the head of the vibrator excites the solid particles in the mix, this "liquifies" the mix and causes it to flow. The concrete does not move uniformly however, the coarse aggregate particles are propelled away from the vibrator head preferentially because of their greater mass. Momentum is transferred through particle collision and mortar then begins to flow between the coarse aggregate. A stationary head does not compact the concrete to any great degree, the vibrator head must be moved up and down in the concrete to facilitate mortar flow and homogeneous mixing. Undervibration is a frequent cause of honeycombing (pockets of large aggregate without mortar between them) since the coarse aggregate has been excited but the mortar did not flow to the same extent.

A vibrator also has a limited "sphere of influence", for uniform compaction it must be inserted into the concrete at close enough intervals that the spheres of influence overlap. The sphere of influence will depend somewhat on the size of the vibrator and the workability of the mix but is typically about 500 mm (18 inch). A vibrator has no influence below the head, when successive lifts are to be vibrated together to eliminate the joint, the head should be completely immersed in the lower lift and drawn slowly through the upper lift.

For ordinary concretes having low to medium workability there is typically no danger of over-vibration, inadequate vibration and the consequent poor compaction and low quality concrete pose a much greater risk. In practice, vibration is carried out as long as the air continues to rise to the surface and the level of the concrete surface around the vibrator or within its radius of action decreases. Fresh concretes with slumps greater than 100 mm typically require very little vibration and true "flowing" concretes with slumps more than 200 mm are usually rodded or tamped rather than vibrated. Vibration of such mixes can reduce the viscosity and cohesion of the paste to such an extent that their stability becomes very low, if the cohesion is too low to hold the aggregate uniformly distributed in the mix, the concrete will bleed and segregate.

8.6 Considerations for the CTBM

Several of the early investigations on extruded lining systems examined the issue of vibration. Foster-Miller(1983) used external vibration in some of their tests but it was not really clear how vibration (or lack thereof) affected the quality of the concrete since they had a number of operational problems in their testing. Parker (1973) stated that external vibration was the only practical way to vibrate steel fiber reinforced concrete but did not give an reason. Doherty et al. (1979) noted that cast in place pipe construction typically uses internal vibration; they mentioned two (vertical stuffing augers and wiggling rebar) but did not give any specifics on how these worked. They also stated that there would be a problem using internal vibration in an extruded lining system because there might be frequent shutdowns or rapid setting concrete might be used. It is not exactly clear why this would be a problem other than in the case of a system shutdown it would be one more component that had to be cleaned.

Clearly a normal poker vibrator could not be used with the CTBM since these have to dropped into the concrete and then pulled out. However, a number of rigid vibrating rods, either horizontal or diagonally inclined, could be incorporated into the bulkhead. The key question is whether vibration is, in fact, necessary. In normal construction, the amount of entrapped air can vary between 5 and 25 % [Bartos, 1992], in the case of the CTBM however there is likely to be little, if any, entrapped air. Rather than being dropped into forms, the concrete is being placed under fairly high pressure, it will tend to be well consolidated just from the placing pressure.

It should be fairly easy to determine whether vibration is necessary by examining the overall quality of the freshly extruded concrete and the microstructure and strength of the hardened concrete. The hardened concrete should also be examined in some detail to determine what effect the placement pressure is having on the microstructure. With normal concrete and under normal placing conditions, the volume of hydration products generated during the first half hour is small, if the concrete is kept in a slow state of agitation or is periodically remixed, it can usually be placed up to 1 1/2 hours after batching. The high early strength required by the CTBM however means there will have to be a rapid generation of hydration products and rapid bonding between them. Once there has been bonding, the force from subsequent concrete placement may cause disruption of the paste structure. This is particularly likely if there is a temporary since the concrete placed previously will have undergone considerable hydration when the machine starts up again. Although a retarder could be applied to the surface of the concrete when a shutdown occurred this would only be effective on the very top layer. Parker et al (1971) examined the microstructure of the concrete produced in their slipform tests and found that there appeared to be no disruption of the paste due to placement pressure. They were using a considerably lower pressure that what is proposed for the CTBM however. In addition, the cement used for the CTBM may not have the same characteristics as the cement they were using (a regulated-set cement which is no longer no available in the United States).

Alternatively, exposure to high pressure after some degree of hydration has taken place may produce a better quality concrete. Typically construction of walls and columns is done in multiple placements or "lifts" of various heights, revibration an hour or two after initial consolidation is sometimes used to improve the bond between lifts. This also helps to remove any cracks, voids, or weak areas created by settlement or bleeding, particularly around rebar. The timing for this is critical however, if the concrete has advanced past initial set, revibrating it can cause serious damage.

Since vibration produces a more fluid mix, it may also reduce friction between the fluid concrete and the slipform. Although this might be somewhat difficult to measure in an actual test of the slipform, a relative measure of its effect could be determined from a simpler geometry. One quite simple test would be to embed a steel plate in the fresh mix and measure the force required to lift it out from a vibrated versus an unvibrated mix. The plate would probably have to fairly large in order for there to be an appreciable difference however and the test would probably have to be done quite a few times in order to average out any other factors.

Chapter 9

Porosity

The mechanical response of a material to different states of stress is determined by the bonding within the material. It was originally thought that the very low tensile strength of cement paste was due to the fact that that the bonding between the C-S-H particles was weak van der Waals forces. It is now recognized that hardened cement paste more closely resembles ceramic materials (which are dominated by ionic-covalent bonding) than it does organic polymers (which are dominated by van der Waals bonding). Although Van der Waals forces are thought to be responsible for the creep and shrinkage behavior of concrete [Mindess and Young, 1981], the low tensile strength of concrete is primarily due to the presence of voids and microcracks in the paste.

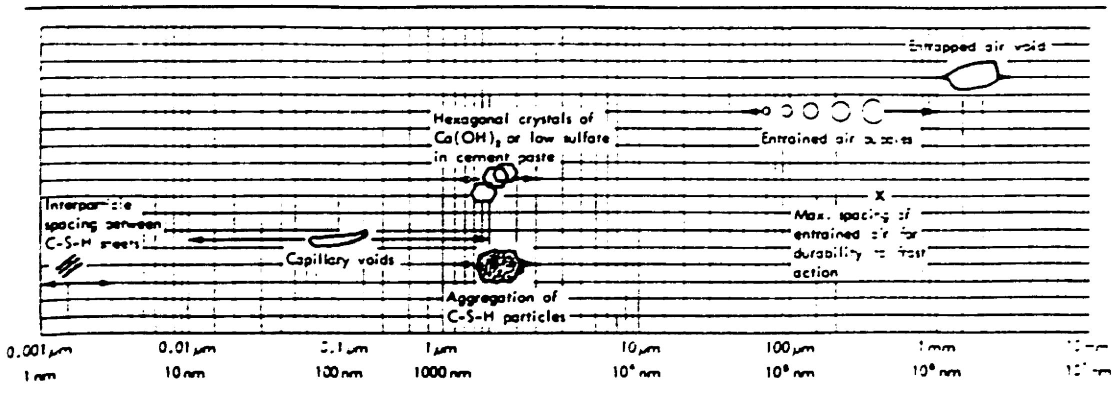
An understanding of the pore structure of a paste is important because most of the properties of concrete (particularly strength and durability) are either directly or indirectly dependent on the porosity of the hardened paste and the pore size distribution. The pore structures in paste are difficult to measure experimentally however. The pores cover an extremely wide range of sizes, from less than 1 nm to over 1 mm in effective diameter, i.e. approximately five orders of magnitude. Although porosity over the whole size range has an influence on paste properties it is difficult to get an exact assessment of pore-size distributions. No one measurement encompasses the whole size range, there is also controversy over how to interpret some of the experimental data.

9.1 Capillary Versus Gel Pores

Pores intrinsic to the cement paste are often divided into capillary pores and gel pores. The capillary pores are the remnants of water filled space that exists between the partially hydrated cement grains, this is the porosity seen in SEM micrographs. The gel porosity on the other hand develops as the C-S-H gel forms and is considered part of the paste. Since it cannot be resolved by a SEM it is included in the volume occupied by C-S-H. Depending on the degree of hydration, capillary pores usually have a diameter between 5 μm and .01 μm (10 nm), gel pores have a diameter between 10 and 1.0 nm. The size division between capillary and gel porosity is to a large extent arbitrary however as there is a continuous spectrum of pore sizes. In addition, some of the gel pores actually qualify as capillary pores according the more accurate definition that a capillary pore is one in which capillary effects can occur (i.e. a meniscus can form.)

As noted in Chapter 5. the C-S-H gel includes a significant amount of pore space. As long as there is enough water to hydrate the cement fully, the total amount of gel porosity is independent of the w/c ratio, it depends only the degree of hydration. Variations in the w/c ratio will thus affect only the capillary porosity, pastes with a high w/c ratio will have high capillary porosities. Since water flows much more easily through larger pores, the permeability of a paste with high capillary porosity may be three orders of magnitude higher than a well hydrated paste with a low w/c ratio. At low w/c ratios the larger pores become isolated and water movement is primarily due to much slower flow through the gel pores. In a mature paste the bulk of the porosity is gel pores within the C-S-H, thus permeability will tend to be low; the water in these voids is strongly held by hydrogen bonding however; its removal may contribute to drying shrinkage and creep.

The volume and size of capillary voids depend on the original distance between cement particles as well as the degree of hydration. Although high w/c ratio pastes may have capillary voids as large as 3-5 μm in early stages, in well hydrated, low w/c ratio pastes they typically range from 10 to 50 nm. Capillary voids greater than 50



Dimensional range of solids and pores in a hydrated cement paste.

Figure 9-1: Relative sizes of Pores [Mehta and Monteiro, 1993]

nm are assumed to be detrimental to strength and permeability while voids smaller than 50 nm are more important with respect to drying shrinkage and creep.

In addition to the gel and capillary pores, the paste may contain entrapped and entrained air bubbles. Entrapped air bubbles are caught in the paste as the concrete is mixed and poured; entrained air bubble are purposefully created (using admixtures) to increase the freeze-thaw resistance of the paste. Both entrapped and entrained air voids are much larger than capillary voids and are capable of adversely affecting strength and permeability. Entrapped air voids can be as large as 3mm, while entrained are voids are typically between 50 and 200 μm (slightly larger than the calcium hydroxide and original cement grains). Although gel and capillary voids are irregular in shape, both entrapped and entrained air voids are generally spherical. Relative sizes of these voids, compared with the solid phases are shown below:

9.2 Classification by Size

Classification by size (rather than method of formation) is actually more useful for evaluating the effect of the pores. The classification system used for many porous materials is:

- \- micropores (<2.5 nm diameter)
- \- mesopores (2.5 - 50 nm diameter)
- \- macropores (> 50 nm diameter)

Capillary pores would thus include some micropores and some mesopores, gel pores would all be micropores. Micropores will have an effect on the intrinsic paste strength as well as the drying shrinkage and creep behavior. Mesopores will effect drying shrinkage and creep, they will also effect mechanical strength by serving as stress concentrators. Macropores will have a strong effect on mechanical strength (fracture characteristics) and transport phenomena (permeability and conductivity).

9.3 Measurement of Porosity

The two main methods used to measure the pore-size distribution of hardened cement paste are mercury intrusion porosimetry (MIP) and physical adsorption of gases (usually either nitrogen or water) at very low partial pressures. MIP involves forcing mercury into the pore system by the application of external pressure. Since mercury does not wet the paste force is needed to overcome surface effects, the pressure required is inversely proportional to the pore radius. Although mercury porosimetry is better for examining the larger capillary pores (those which influence permeability and shrinkage at high humidities), adsorption studies give a more complete measure of the gel porosity and the small capillaries. In the overlapping size range, data from the two methods do not always agree very well however. In addition, adsorption processes using different gases may give different results.

These methods are all limited by the fact that a pore geometry has to be assumed. Although cylindrical pore geometry is typically assumed, SEM micrographs show that both capillary and gel pores are highly irregular and may have restricted size entryways. An even more important problem with these methods is that the cement paste must be strongly dried before measurements can be made. Since C-S-H undergoes significant changes on drying, it is probable that changes in the pores-size distribution occur. In particular, it is thought that micropores collapse to form mesopores. This can be minimized but not eliminated by using solvent replacement drying in which methanol is allowed to replace water by diffusion processes. Thus these methods do not really give absolute values regarding pore structures, they are more useful for comparing different pastes.

Recently, nuclear magnetic resonance relaxation spectroscopy has been used to examine the pore structure of undried pastes by looking at the mobility of water in different pore [Young, 1992]. Computer simulation can also provide a description of the pore structure of an undried paste, such simulations have been used to predict transport properties. Hardened paste can be analyzed qualitatively by analysis of polished sections using back scattered electro imaging; this can be used to determine the degree of hydration and the relative amounts of C-S-H and calcium hydroxide.

9.4 Calculation of Porosity

As with many porous materials, the strength of a cement paste depends strongly on its porosity, the chemical formula of the hydration products is typically less significant. Theoretically, the total porosity in a paste could be calculated from the hydration equations, using the specific gravities of each species. This is not really practical however since the C-S-H varies in composition, in addition both the compound composition of the cement and the rate of hydration of the compound can vary. As a result, empirical equations based on the amount of hydration were developed. In these equations, the hydrated cement fraction is considered to include all of the hydration products (C-S-H, calcium hydroxide and sulfoaluminates), without distinguishing between them. In addition, water in the paste is considered to be either evaporable or nonevaporable. Evaporable water is held in capillary and gel pores and is lost when a saturated paste is dried; although it is primarily associated with the C-S-H, it includes some hydrate water from the calcium sulfoaluminates. Nonevaporable water is the structurally combined water in the hydration products, it is not lost unless a dried paste is ignited to 100 °C.

The nonevaporable water (W_n) is proportional to the the amount of hydration:

$$W_n = .24\ \alpha \text{ g/g of original cement}$$

where α is the degree of hydration. When the cement is fully hydrated ($\alpha = 1.0$) there are .24 grams of nonevaporable water combined with each gram of cement. The degree of hydration can therefore be calculated from a measurement of the nonevaporable water. Once the degree of hydration is known, the gel and capillary porosities can be calculated.

The bulk density of the hydration products is considerably lower than the density of anhydrous cement grains due to both the incorporation of water and the increase of porosity; on complete hydration, 1 cm^3 of cement requires approx 2.2 cm^3 of space for its hydration products. Since the specific gravity of cement is approximately 3.2, one gram of cement occupies .31 cm^3. On the basis of the ratio given above (1:2.2), .31 cm^3 (one gram) of cement when hydrated occupies .68 cm^3. Therefore the volume of hydration products V_g is given by:

$$V_g = .68\ \alpha \text{ cm}^3 \text{ / g of original cement}$$

In a saturated paste, the water in the gel pores is equal to:

$$W_g = .18\ \alpha \text{ g/g of original cement}$$

Since the specific gravity of water is 1, the volume of gel porosity (P_g) in a saturated paste can be determined by dividing the amount of gel water by the total volume of the hydration products:

$$P_g = W_g / V_g = .18 / .68 = .26$$

Thus about one-fourth of the volume of C-S-H is pore volume, this value is essentially a constant for all normally hydrated cements,. The capillary porosity (P_c) is given by:

$$P_c = w/c - .36 \text{ a cm}^3/\text{g of original cement}$$

where the w/c ratio is by weight. If a w/c ratio of .36 is used, at complete hydration ($\alpha = 1$), capillary porosity will be zero. Before hydration starts the capillary porosity is equal to the w/c ratio, i.e. at a w/c ratio of .5 there are initially .5 cm^3 of water-filled voids per gram of cement.

As noted above, these equations are approximations since they do not distinguish between either the cement compounds or the hydration products. Actual values for specific gravities and the amounts of structurally combined water will vary somewhat. As an example, the density of C-S-H is approximately 2.0 g/cm^3 whereas calcium hydroxide is approximately 2.25 g/cm^3. The specific gravity of the paste will therefore depend on the relative amounts of the hydration products. Nevertheless, these equations are useful for understanding some of the properties of the paste.

Another quantity sometimes used as a measure of capillary porosity is the gel/space ratio (X) defined as the volume of gel (including gel pores) divided by the volume of gel plus the volume of capillary pores:

$$X = .68\,\alpha \,/\, (.68\,\alpha + w/c - .36\,\alpha) = .68\,\alpha \,/\, (.32\,\alpha + w/c)$$

9.5 Durability

The term "durability of concrete" refers to its service life under given environmental conditions and is primarily a function of the impermeability or watertightness of the concrete. As noted above, the permeability of a concrete is a function of its porosity, i.e. the amount, size and continuity of its capillary pores. The porosity is to a large extent determined by the w/c ratio (a measure of the original capillary space between particles) and the degree of hydration. With increasing hydration there is an increase in the amount of C-S-H and thus an increase in the amount of gel porosity. Since these pores are extremely small and not interconnected they do not contribute significantly to the permeability. The permeability of a mature paste in fact decreases due to a reduction in the capillary porosity.

One other factor influencing porosity is that anhydrous cement particles have a tendency to attract each other and form flocs which entrap large quantities of mixing water. These regions of locally high water-to-cement ratio will cause an increase in the capillary porosity in the system; a flocculated cement results in a very heterogeneous, nonuniform pore system. In a well dispersed system (i.e. one in which a water reducing agent has been used) the size and shape of the pores will be much more uniform, this tends to produce a paste of much higher quality. Water reducing admixtures will be discussed in more detail in Chapter 10.

The addition of mineral admixtures such as fly ash, silica fume and slags can modify the microstructure of the hardened paste. Fly ash and silica fume in particular react with calcium hydroxide to form additional C-S-H. This increases the volume fraction of C-S-H which tends to increase the proportion of micropores to capillary pores and generally creates a finer pore structure with reduced interconnectivity.

Silica fume is particularly effective because its small physical size allows it to pack between the cement particles, thus further reducing the size of the pores. One of the principal reasons for using silica fume in a lot of concretes is its ability to decrease the permeability of the concrete through its effect on the pore structure.

Chapter 10

Chemical Admixtures

A basic concrete mix consists of three major components: aggregate, cement and water. In practice however, many of the properties of concrete may be determined by chemical admixtures added in very small amounts during mixing. Almost every property of concrete can be modified to some extent, as a result there is an enormous number of products, many of them proprietary, marketed as admixtures for concrete.

Admixtures give the mix designer considerable control over the properties of both fresh and hardened concrete. They can be used to improve workability (increase slump), accelerate or retard setting times, control strength development, reduce thermal cracking, increase resistance to chemical attack or reduce freeze-thaw deterioration. In addition, admixtures can be particularly useful for applications like the CTBM where it is important that behavior of the concrete be consistent. Since the chemical reactions that occur during the manufacture of the cement clinker cannot be completely controlled it is extremely difficult to create a cement to exact specifications. The initial ingredients will always vary slightly in both composition and gradation and there will always be some impurities. Even the same ingredients reacting at the same temperatures can result in slightly different products.

Specifications for admixtures are given in ASTM C494, *Chemical Admixtures for Concrete.* The basic types of admixtures are: air entrainers, water reducing agents, accelerators and retarders. Many admixtures however are formulated to have more than one effect, i.e. both water reducing and accelerating.

In terms of the way they act, admixtures can either be surface active chemicals (surfactants) or ionizing chemicals. Surface active chemicals act on the cement-water system by reducing the surface tension of water and reducing attractions between cement particles. They are typically long-chain organic molecules with polar (electrically charged) side groups. The side groups for concrete admixtures tend to be anionic (negative) since these are less expensive; among the most commonly used are -COO^- and SO_3^-. The period of effectiveness of a surfactant is rather limited because soon after the start of hydration large amounts of hydration products, particulary ettringite, begin to form. These hydration products tend to engulf the small quantity of surfactant present. The temperature of the concrete and the cement fineness and composition, particulary the C_3A, SO_3^- and alkalis control the rate of ettringite formation, consequently they will affect of cement-admixture interactions. Air entrainers, water reducers and superplasticizers are surfactants.

Ionizing chemicals dissolve in the pore water and affect the hydration of the cement particle; they are used to control set time and strength development. Typically they affect the solubility of the cement constituents (and thus their reactivity) by altering the amount and type of ions in the pore solutions.

10.1 Air Entrainers

Air entraining agents consist of a non-polar hydrocarbon chain with polar (charged) groups at one end. The polar groups cause this end of the molecule to be hydrophilic (water attracting). At air-water interfaces the polar groups are oriented towards the water which lowers the surface tension. This both promotes formation of air bubbles and counteracts their tendency to coalesce. At the solid-water interface (the surface of the cement particles) the non-polar groups are oriented towards the water. This makes the cement surface hydrophobic (water repelling); air bubbles can displace water and become attached to the cement. Commonly used air entrainers include salts of wood resins, proteinaceous materials, petroleum acid and synthetic detergents.

Although the most important use of air-entrainers is to reduce freeze-thaw damage to the concrete, a side effect is improved workability, particulary in low cement mixes. In their early tests, Foster-Miller(1983) experimented with some mixes containing air entrainers. Given that freeze-thaw damage is probably not a major concern within a tunnel environment it does not seem necessary to use an air-entrainer in the CTBM mix. Large amounts of entrained air will cause a reduction in strength due to the increased porosity and pumping is less efficient since a certain amount of the piston stroke is used in compressing the air. Furthermore, since air-entrainers make the cement particles hydrophobic, an accidental overdose can cause severe retardation.

10.2 Water-Reducing Concrete Admixtures

Water reducing admixtures are used for two reasons. One is to increase the workability of a mix (as measured by tests such as slump, compacting factor or Vebe) without adding water. The other is to achieve higher compressive strength without increasing the cement content - for a given workability, the amount of water and thus the w/c ratio can be reduced, this results in a stronger concrete. It is also possible to achieve both effects with an appropriate change to the mix design, i.e. a concrete could be formulated with a w/c ratio of .4 instead of .45 and therefore have a higher compressive strength but because of the water reducing agent still have a higher slump.

The most basic rule in structural concrete mix design is that the water content should be as low as possible while still producing a concrete that can be placed and compacted. Both the strength and durability of a concrete are inversely related to its water content. The volume change in hardened concrete is also greatly influenced by the amount of water in the original mix, as the water content increases, so does the tendency for drying shrinkage and creep.

In terms of construction however, high workability makes it much easier to place and compact the concrete. When cement powder is added to water, the cement particles will tend to cluster together and form flocs (referred to as flocculation.) This is due to the characteristics of both cement and water. Water possesses high surface energy and in general does not mix well. In addition, when crystalline materials such as cement are finely ground, the surfaces will tend to have residual charges, some negative, some positive. As cement is mixed with water attractive forces between particles cause them to flocculate. A large amount of water can be caught in these flocs, in addition the attractions between cement particles create resistance to movement. Thus additional water is necessary to cause the mix to flow.

Water reducing agents are negatively charged chemicals that get absorbed on the surface of the cement particles. They impart a strong negative charge to the particles which both reduces the tendency for flocculation and breaks up flocs already formed. The most significant result of this deflocculation is that more of the mix water is available to the system, thus less water is required to achieve a given workability or alternatively more workable concrete can be obtained from a given water content.

There are two types of water reducing admixtures: water reducers (also called plasticizers) and superplasticizers (also called high range water reducers). Even though they act in somewhat the same manner, they are chemically quite different and have different side effects. As defined by ASTM C494, water reducers as those chemicals which, when added to a concrete mix, will produce the same slump with between 5 and 12% less water. Superplasticizers must produce the same slump at over 12% less water. Although a reduction greater then 12% can be produced by severely overdosing a water reducer, the side effects associated with high dosages make this impractical.

Water reducing agents also cause the cement particles to be more evenly dispersed. Since the growth of cement hydrates is largely a surface effect this can lead to a greater rate of hydration, it also produces a more uniform hydration product. More uniformity on the micro scale, particulary the absence of areas with locally high w/c ratios, tends to translate to higher strength and more durable concrete. Finally, since all of the cement particles are negatively charged there are less inter-particle attractions, thus less energy is required to place and compact the concrete. Even though water reducing agents do produce a well dispersed system, some water reducers interfere with hydration by virtue of the fact they are absorbed on the surface of the cement particles. This will result in an overall retarding effect.

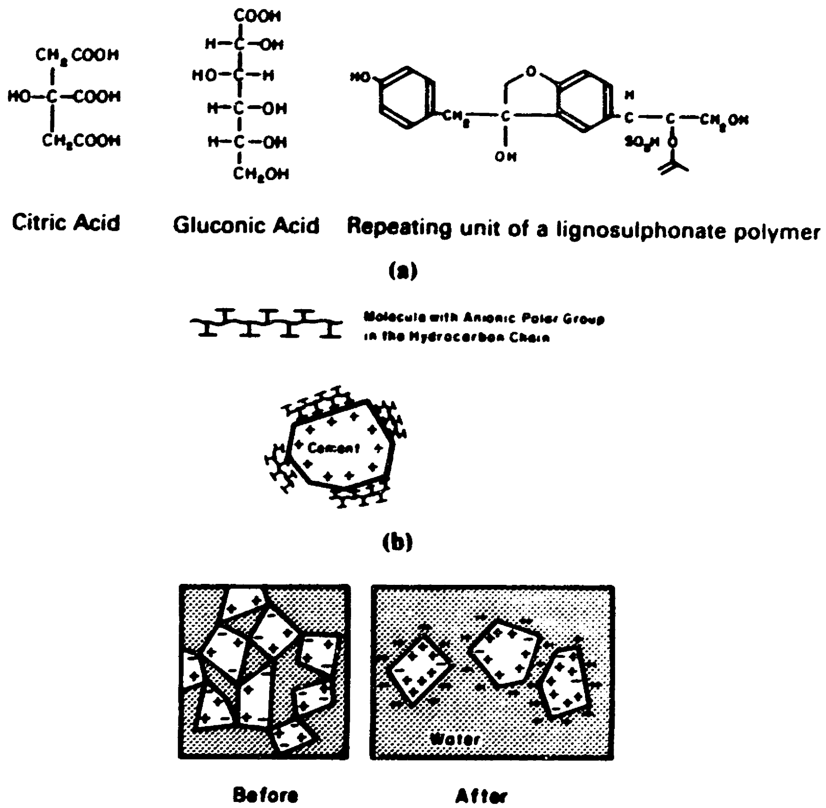


Figure 10-1: Effect of Water Reducing Admixtures [Mehta and Monteiro, 1993]

10.2.1 Water Reducers

The chemical structure of most water reducers is similar to that of air entrainers except that the anionic polar group is attached to a hydrocarbon chain which is itself negatively charged (and thus hydrophilic) due to the presence of OH^- groups. The traditional basis for water reducers admixtures is lignosulfonic acid, in the form of either its calcium or sodium salt. This material is a by-product of wood pulp industry; non-retarding admixtures are formulated from a purified product which has the bulk of the sugars and other impurities removed. The effects of calcium lignosulfonates have been studied in some detail; although they appear to slightly decrease the rate of cement hydration, they typically do not alter the hydration products [Hewlett, 1988].

Water reducers can also be formulated from synthetic raw materials. Since the chemical compositions of these materials can be controlled through their manufacturing process, their effect on hydration can be more closely controlled. They tend to be significantly more expensive than lignosulfates however.

10.2.2 Retarding Water-Reducing Admixtures

Some water reducers are designed to be retarding. These products are normally based on hydroxycarboxylic acids which contain a considerable number of hydroxyl groups; when absorbed on the surface of the cement they tend to retard initial hydration reactions. Lignosulfates of low purity (i.e. still containing wood sugars) are also used sometimes.

After the initial retardation, strength development of a retarded mix is similar to that of a non-retarded mix. Materials of this type however can have a much higher dispersing effect (hence water reducing capability) than normal water reducers, with the lignosulfate this is probably due to the fact there is a higher concentration of solids in the formulation [Hewlett, 1988].

Excessively large amounts of any water reducer may retard set by preventing the hydration products from forming bonds. Thus, depending on dosage, most water-reducers can also serve as set retarders,. Even though set may be delayed however, early strength after set may be somewhat higher due to better dispersion of the cement particles. Some water reduces also contain an accelerating agent such as triethanolamine to offset the retarding effect.

10.2.3 Superplasticizers

Compared to water reducers, relatively large amount of superplasticizers can be used without causing excessive bleeding or set retardation. Thus, for a given w/c ratio a much greater increase in workability is possible, alternatively, for a given workability a much lower w/c ratio can be used. A concrete with a cement content of 360 kg/m^3 and a w/c ratio of .45 had a slump of 30 mm (1.25") without superplasticizer, with superplasticizer, slump increased to 225 mm [Mehta and Monteiro, 1993].

Superplasticizers are usually sulfonated salts of either melamine or naphthalene formaldehyde condensates. These are long chain, high-molecular weight (20,000 to 30,000) compounds with a large number of anionic groups. When adsorbed on a cement particle they impart an extremely strong negative charge to the particle. As noted above, this will cause the cement to deflocculate, releasing trapped water and exposing additional surfaces for hydration.

In order to obtain the required high early strength, the concrete used with the CTBM will probably have a very high cement content and a low w/c ratio, a superplasticizer will almost certainly be needed to make the concrete pumpable. Superplasticizers are typically sold as solutions of approximately 40% solids. Typical dosages of superplasticizers are 1 to 2% by weight of the cement, this comes out to 16 to 32 ounces per 100 pounds cement [Berke, 1994].

Superplasticizers are to a large extent replacing accelerators as a means of producing high early strength in pre-cast applications. This is due to concerns both with corrosion and quality of the product. Superplasticizers allow the use of a lower w/c ratio which means both higher early strength and higher ultimate strength.

10.3 Set and Strength Controlling Chemicals

The way in which accelerators and retarders work is not completely understood, in part because the processes involved in the hydration of cement are not well understood. A number of theories have been proposed, most of them are related to the rate and method of dissolution of the cement grains. Many also believe there are physical effects involved, i.e. retardation can result if the hydration bonds are physically prevented from forming. It is likely that there are actually several mechanisms, perhaps varying in significance with different types of chemicals.

It is generally believed that the initial reactions of cement with water are through-solution: the compounds first ionize and then the hydrates form in solution; due to their limited solubility, they crystallize out. The stiffening, setting and hardening of cement are the result of the progressive crystallization of the hydration products. While it is possible to influence both the ionization and the crystallization with admixtures, the action of a set-controlling chemical is usually attributed to its effects on ionization. When considering the effect of these admixtures, it is helpful to view the cement as being composed of various acidic ions (primarily silicate and aluminate) and a base ion (calcium). The solubility of each will depend on the type and concentration of the acid and base ions present in solution.

An accelerating admixture must promote the dissolution of the cement grains, in particular, it must promote the dissolution of the silicate ions since these dissolve at the slowest rate during the early hydration period. A retarding admixture on the other hand must impede the dissolution of the cement, in particular it must impede the aluminate ions since these dissolve at the highest rate during the early hydration period.

Some chemicals act as retarders when used in small amounts (eg .3% by weight of cement) but as accelerators when used in larger amounts (1% or more by weight). A strong cation in the solution (i.e. K^+ or Na^+) reduces the solubility of a less strong cation like calcium but tends to accelerate the solubility of silicate and aluminate ions. In small concentrations, the former effect is dominant, in large concentrations, the latter effect becomes dominant. A strong anion in solution i.e. Cl^-, NO_3^- or SO_4^{2-} reduces the solubility of less strong anions (i.e. silicates and aluminates) but tends to accelerate the solubility of calcium ions. In small concentrations, the former effect is dominant, in large concentrations, the latter effect becomes dominant.

10.3.1 Accelerating Admixtures

In addition to their effect on the dissolution of the cement grains, accelerators may further increase hydration by altering the coating that develops around hydrating grains. When cement is mixed with water, the initial reactions are between the gypsum and the C_3A, resulting in the formation of ettringite. At the same time however, calcium hydroxide is dissolving from the major chemical constituent of the cement, the tricalcium silicate C_3S, leaving a surface which is rich in silicic acids. The dissolution of calcium hydroxide rapidly increases the pH of the pore solution. As the pH rises towards 13, a chemical reaction occurs between the calcium and hydroxyl ions in solution and the silicic acids, resulting in the formation of calcium silicate hydrate (C-S-H). Together with calcium hydroxide, which is formed at the same time, and ettringite, the C-S-H forms a coating around the hydrating grain.

Subsequent hydration decreases to a very low level, producing what is known as the dormant period. Significant strength development does not start until the end of the dormant period.

Normal accelerators (as distinct from set accelerators) are thought to affect these reactions in some way, either by producing a more permeable coating or by diffusing through the coating and forcing out OH^- to maintain charge balance. An increase in OH^- in solution presumably forces further production of C-S-H and thus increases the rate of strength development.

A number of chemical will accelerate Portland cement hydration. These can be divided into three groups, depending on the active constituents:

- anionic materials (materials based on the action of the a negative ion)
- cationic materials (materials based on the action of the a positive ion)
- organic chemicals

Most commercial accelerators anionic materials, the most common being calcium chloride. Non-chloride based chemicals include formates, nitrates, nitrites and thiocyanates. Generally the calcium salts of these materials are the most effective but very soluble salts such as sodium are also used. A number of other materials such as thiosulphates, permanganates and chromates have been suggested as effective accelerators but are less used commercially. Some of these same chemicals have been tried as ingredients of rapid-set, high early strength cements.

Typically it is not the cation in a compound which is responsible for accelerating effects. As mentioned above however, the cation can have an effect on the power of an anion, calcium salts are generally the most effective. There have been reports of trivalent cations such as aluminum or iron(III) being significant in the performance of a particular chemical, however it is also noted that these materials tend to be difficult to control and can result in premature stiffening, as a result they are rarely used in commercial formulations. [Hewlett, 1988]. Although lithium carbonate has used as an accelerator for aluminous cements with the lithium ion Li^{++} being the effective ion), it is not used commercially as an accelerator for portland cement. Various other forms of lithium (i.e. lithium oxalate) have also been suggested as possibly effective but they are not used commercially.

The best known and most widely used organic accelerator is triethanolamine (TEA). TEA is usually only a small part of a formulation however. Its effect is very sensitive to dosage and the chemical composition of the cement, consequently it is rarely used as the sole component of an accelerator. Its most common usage is in the formulation of water reducers where it counteracts the retardation the water reducing chemicals produce. TEA affects both C_3S and C_3A and consequently can have a quite variable effect on concrete. When used in high level it can cause considerable retardation, with some cements on the other hand it may cause flash setting.

Temperature can be important with respect to the performance of accelerators; accelerators which are very effective at 20 °C may be of little use at 5 °C. The converse is also possible, some accelerators, i.e. calcium chloride are more effective in percentage terms at low temperatures. At 20 °C, the rate of strength development is not significantly increased by adding $CaCl_2$.

Set Accelerators versus Strength Accelerators

When considering concrete accelerators it is necessary to distinguish between those which are set accelerators and those which are strength accelerators. Set accelerators basically accelerate just initial set, they do so through the rapid development of ettringite. Strength accelerators however accelerate the entire hydration process which means both accelerated setting times and increased strength at early ages. An admixture marketed as a set accelerator may not necessarily increase strength at early ages, it may in fact have the opposite effect. An example is triethanolamine which accelerates tricalcium aluminate (C_3A) hydration but retards tricalcium silicate (C_3S) hydration. Accelerated stiffening occurs because the reaction between gypsum and C_3A which produces ettringite is accelerated. There is no significant strength development until the C_3S begins to hydrate however, since this reaction is retarded there will be a delay in final set and an overall decrease in early strength.

Set accelerators are used where a small amount of strength is needed very rapidly. This includes shotcrete in tunnel and repair of marine facilities. In the latter application, set time is often more important than strength as the concrete may be required to resist wave action within a short time of placement. Many set accelerators are based on either silicate or aluminate ions, the rapid stiffening which results is due to the formation of large amounts of ettringite.

Calcium Chloride

Calcium chloride $CaCl_2$ has been an accelerator for concrete since at least 1885; it remains the most widely used. It appears to be uniquely effective in its ability to accelerate both initial set and early strength development without significantly affecting ultimate compressive strength. In addition to being the most effective material on a percentage basis, it is also the cheapest.

The mechanism by which calcium chloride works is not really understood. Although it reacts relatively rapidly with tricalcium aluminate, in cement this reaction is inhibited by gypsum. The chloride ion is thus left free to catalyse the tricalcium silicate reactions. One of the possible mechanisms is that the chloride ion becomes temporarily incorporated into the early calcium silicate hydrate (C-S-H). Because of the high charge density and mobility of the chloride ion, the coating around the hydrating grains would have a more open and porous structure. This allows a greater exchange of water through the coating with fresh water passing into the cement grain and the silicate solution out [Hewlett, 1988]. It has also been proposed that again due to its high mobility, the Cl- is able to diffuse through the coating more rapidly than other ions and that OH- ions are then forced out to maintain charge balance. This forced diffusion of the OH- ion presumably accelerates both the precipitation of calcium hydroxide from the pore solution and the decomposition of calcium silicates from the cement grains. [Diamond, 1980]

Acceleration is proportional to the amount of $CaCl_2$ added, typical dosages are 1.5 to 3% by weight of the cement. $CaCl_2$ is normally supplied by admixture companies in the form of a 30-35% solution of anhydrous $CaCl_2$ which is equivalent to approximately 20% chloride ion.

The effectiveness of $CaCl_2$ may be partly due to the fact that, in the proportions used it is entirely soluble in water and it remains dissolved in the pore solution for at least the first three hours. The presence of such a large amount of electrolyte in the pore solution presumably has a significant effect on the hydration processes. Adding $CaCl_2$ causes a considerable increase in the Ca^{++} concentration and a decrease in the pH (presumably due to a common ion effect with the Ca^{++}), it also causes a significant increase in the ionic strength of the solution (when 3% $CaCl_2$ is added there is an order of magnitude increase in the ionic strength of the solution) [Diamond, 1980].

Although some chloride will be incorporated into the C-S-H gel and small amounts of monochloraluminate may be formed, it appears that he acceleration is not due to the formation of new products, rather that $CaCl_2$ accelerates the formation of the compounds normally found in cement paste. The C-S-H paste tends to have a more reticulated or honeycomb morphology than that found in a non-accelerated paste however, this same structure is produced when there is a high level of impurities in the cement. There is also some evidence to suggest that the effective pore diameter distribution is changed by the addition of calcium chloride, typically there are a greater proportion of large pores [Hewlett, 1988].

A number of studies have indicated that mature $CaCl_2$ containing concrete undergoes significantly greater drying shrinkage and marked increases in creep rates especially in environments with less than 35% RH and when loaded at early ages. It is thought that this effect is due to the difference in the structure of the hydration products; calcium chloride is thus not recommended in creep-sensitive situations. Although ultimate compressive strength appears to be unaltered, tensile and flexural strengths are typically somewhat lower, in addition sulfate resistance is lower [Diamond, 1980]. Finally, the use of calcium chloride means that there is a substantial increase in the number of unbound or loosely-bound chloride ions in the paste, depending on the environment and the cement, this may substantially increase the risk of corrosion.

Chloride Free Accelerators

Chloride free-accelerators such as those based on formates and nitrites are used where corrosion is a concern. They are generally less effective and more expensive than calcium chloride, it should also be noted that "chloride free" does not automatically mean the admixture will not increase the risk of corrosion. If corrosion is a concern, the materials should be tested under job conditions to ensure that there are no problems.

Compared to calcium chloride, there is relatively little data available on the effects of chloride-free accelerators. What information has been published has usually been based on tests done by the admixture manufacturers under their own specified test conditions, therefore it is hard to make comparisons. In particular, materials with different chemical bases may produce optimum performance under different sets of conditions.

Calcium nitrite, a chemical marketed by many companies as a corrosion inhibitor, is also a fairly strong set accelerator. One such calcium nitrite based product is Darex Corrosion Inhibitor (DCI) from W.R. Grace. This was used on several of the SHRP tests [Leming, 1993] and was found to significantly accelerate set time. It was not entirely clear from their data whether early strength was significantly accelerated. Accelerated set times means of course that the concrete is workable for a shorter period of time - the SHRP investigators found that the concrete was only workable for about 15 minutes after the DCI was added, as a result they needed to add it at the job site.

10.3.2 Retarders

As noted above, retarders can affect the hydration process by decreasing the solubility of the cement ions. Some chemicals further inhibit hydration by forming insoluble and relatively impermeable coatings around the hydrating particles. The calcium salts of phosphoric, boric, oxalic and hydrofluoric acid for example are highly insoluble and readily crystallize out in the vicinity of hydrating particles. Once an insoluble and dense coating is formed around a cement grain, hydration slows down considerably. Phosphates are a common constituent of many commercial set-retarding admixtures. Admixtures can also act as retarders by other mechanisms: surfactants such as gluconates and lignosulfates physically delay set by preventing bond formation among the hydration products.

Most retarders are only effective through initial set, once a certain level of hydration is reached, hydration will continue at the normal rate and sometimes even more rapidly than normal. Although retarders are sometimes used in an effort to reduce the heat of hydration, there is no evidence to suggest that they actually reduce the total amount of heat generated, furthermore if a retarder is simply preventing the hydration products from forming bonds (as opposed to preventing hydration), it will not have a significant effect on the rate of heat generation [Hewlett, 1988].

10.4 Evaluating Admixtures in General

The ASTM specifications for admixtures are primarily performance specifications rather than controls on composition. In most cases admixtures are a complex mixture of compounds and determining their exact chemical constitution is a difficult if not impossible task. Many admixtures are partially derived from industrial waste products hence their composition may vary. There have been a considerable number of problems due to both the misuse of admixtures and to unforeseen interactions between admixtures. Most admixtures affect several concrete properties, all of the effects of an admixture should be taken into account, particularly if some of them are unfavorable. When evaluating an admixture, the following issues must be considered:

a.) the main effect of the admixture on concrete performance.

b.) any additional effects the admixture may have, beneficial or detrimental

c.) the presence of any potentially detrimental substances (i.e. chlorides, sulfates, sulfides, phosphates, sugars, nitrates and ammonia)

d.) physical properties and pH of the material e.) concentration of the active ingredient

f.) procedures for preparing the admixture and adding it to the mix

g.) recommended procedures for storing the admixture / shelf life

It is important to be aware of the manufacturer's recommendations for dosage and well as the maximum permissible dosage and effects of overdosage. It is even more important however that tests be run using job materials under job conditions. The precise effect of an admixture may vary with the cement composition, aggregate characteristics and impurities, mix proportions or presence of other admixtures. The type and length of mixing, time of addition, concrete temperature and curing conditions can also be important.

Procedures for accurate batching of the admixtures must be established. Dosages of some admixtures may be less than 0.1% by weight of the cement, in such cases, overdose can easily occur with potentially disastrous consequences. Finally but most importantly any potential safety hazards associated with an admixture should be known.

10.5 Evaluating What is Needed for the CTBM

The two basic requirements of the concrete used for the CTBM is that it have a high early strength and be pumpable. In order to achieve the required strength, it will probably be necessary to use both a high cement content and a low w/c ratio, consequently, a superplasticizer rather than a water reducer will be probably necessary in order to produce a pumpable mix.

One possible problem with using a superplasticizer is that after a given period of time, typically 15 to 30 minutes depending on both the cement and the particular chemical, there is usually a rapid slump loss; the concrete essentially reverts back to its original slump (i.e. what it would be if a superplasticizer had not been used.) Presumably this is because the superplasticizer becomes incorporated in the hydration product and is no longer available to the system. The behavior of the system with respect to slump loss needs to be examined in detail, particularly at the possible temperature extremes and with several different samples of cement. The ramifications of rapid slump loss should also be examined both as it affects the ability to place and compact the cement and what would happen in case of machine stoppage.

Several superplasticizers currently on the market are formulated to avoid this rapid slump loss by also acting as set retarders. Known as extended-slump life superplasticizers, they are used particularly on large pours where the retarder can help avoid cold joints. Given that, under normal conditions, the concrete in the CTBM will be placed very soon after mixing, there seems to be no need to retard the set. These admixtures cause a substantial increase in set times and since strength gain essentially begins at final set, they cause a decrease in early strength. Early tests by Parker (1971, 1973), Foster-Miller (1979), Maser et al. (1983) included the use of citric acid as a retarder. This, however, was due to the fact that the cements they were using (reg-set and VHEC) had extremely fast setting times, citric acid delayed the set time enough to make the concrete pumpable.

It is not clear whether an accelerator will be necessary for the CTBM. If it is possible to achieved the desired early strength without an accelerator, it would be better not to use one. Using an accelerator means there is the possibility for incorrect dosage, too high a dosage may have a negative impact on the quality of the concrete, too low a dosage may be disastrous. In addition, there can be a problem with making sure an accelerator is evenly distributed in the mix. Accelerators are often avoided in vertical slip-form construction; it is felt that they are dangerous due to the possibility of uneven rates of sets in different locations [Scanda, 1993]. If an accelerator is necessary, it should be tested quite thoroughly under actual job conditions, with the actual proposed mix. In addition, its long term effects with respect to creep and shrinkage should be determined. If calcium chloride is considered, the potential for, and consequences of, increased corrosion must be considered.

It should also be noted that if proprietary cements are used, it may be necessary to use admixtures from the same company. As an example, Cement Manufacturing Company, the company that markets Rapid Set cement, also markets admixtures including Rapid Set Accelerator and RapidSet Set Control (a retarder). There may be an issue of liability and/or performance if admixtures from another manufacturer are used.

Chapter 11

Mineral Admixtures

Mineral admixtures are finely divided siliceous or siliceous and aluminous materials which are usually added to concrete in relatively large amounts (10-100% by weight of the cement). Cements which have additional minerals either interground or blended in during production are common in Europe, slag cements account for approximately one quarter of the total cement production in Germany, pozzolan cements account for approximately one third of the total cement produced in Italy [Mehta and Monteiro, 1993]. They have not caught on in the United States, however. ASTM C 595, *Standard Specification for Blended Hydraulic Cements*, contains specifications for five classes of blended cements but commercial production is extremely limited. There is a growing interest in using mineral admixtures however, i.e. adding these materials at the time the concrete is mixed. Although they are often used to reduce the cost of the concrete, they can also be used to increase the workability of the concrete or reduce the potential for thermal cracking, alkali-aggregate expansion and sulfate attack.

Mineral admixtures are typically classified as cementitious, pozzolanic or both cementitious and pozzolanic. A pozzolanic material is one which by itself possesses little or no cementitious value but which will, when finely divided and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form cementitious compounds. In particular, it forms a calcium silicate hydrate similar to that formed by the hydration of C_3S.

Pozzolanic materials derived from volcanic rocks and minerals occur naturally in many parts of the world. They come from magmas which cooled quickly and formed an aluminosilicate glass with a disordered structure. Due to its disordered structure, the glass is unstable if exposed to lime. Because dissolved gases are simultaneously evolved, the solidified matter tends to be porous with a high surface area, this facilitates the subsequent chemical attack. There are also naturally occurring cementitious materials (i.e. argillaceous limestone). The most common mineral admixtures however are industrial by-products, in particular, fly ash, silica fume and granulated blast furnace slag. Silica fume and some fly ashes are pozzolanic, blast furnace slag is cementitious and some fly ashes are both cementitious and pozzolanic.

11.1 Pozzolanic Material

Pozzolanic activity is primarily due to the presence of amorphous, reactive silica. The pozzolanic activity of a material can be estimated by measuring the strength developed when the material reacts with pure calcium hydroxide at 23 °C for 1 day and then at 55 °C for 6 days. The specifications for these tests are given in ASTM C 595. The reaction between a pozzolan and calcium hydroxide, called the pozzolanic reaction, is shown below:

$$\text{Pozzolan} + \text{CH} + \text{H}_2\text{O} \rightarrow \text{C-S-H}$$

The pozzolanic reaction is significant because it is slower than the C_3S hydration reaction, therefore the rates of heat liberation will be slower (this nominally means that strength development will also be slower). In addition it consumes, rather than produces, calcium hydroxide which is important for resistance to chemical attack. What is typically most important however is that capillary voids are either eliminated or reduced in size as large CH crystals are replaced with C-S-H of a lower density. This increases both the ultimate strength and the impermeability of the system.

The pozzolanic reaction has a significant effect on the microstructure of the cement paste. The formation of secondary hydration products (mainly C-S-H) around the pozzolan particles fills the large capillary voids with a porous, low density material; this transformation of a system containing large capillary voids into a system containing numerous fine pores is referred to as "pore-size refinement". The pozzolan particles also serve as nucleation sites for calcium hydroxide so that instead of large oriented crystals, there are numerous small, crystals and some poorly crystalline reaction products; this process is referred to as "grain-size refinement".

In addition to reactive silica, many slags and pozzolans contain reactive alumina which combines with calcium hydroxide to form calcium aluminate hydrates such as C_4AH_{13}. Other aluminate hydrates may form, depending on the amount and reactivity of the alumina. These aluminates will all tend to react expansively with sulfate to form ettringite; if a pozzolan is being used to improve sulfate resistance, a material low in alumina should typically be used.

Since most mineral admixtures are industrial by-products, their mineralogic composition as well their particle size, shape and grading can vary; some may also contain considerable amounts of inert impurities. As a result, their reactivity and their effect on strength development and heat generation can vary. Their reactivity can also vary depending on the composition of the cement, the ambient temperature and chemical admixtures. Any predictions about their effect on concrete must therefore be made in very general (and qualified) terms.

11.2 Fly Ash

Fly ash is the most widely used mineral admixture; it is a finely divided residue that results from the combustion of pulverized coal. During combustion, most of the volatile and carbon are burned off, the mineral impurities such as clay, feldspar, quartz and shale fuse in suspension and are carried away in the exhaust gas. The fused material cools and solidifies into spherical particles known as fly ash which is then collected by electrostatic precipitators. Typically no further processing is needed for it to be used as an admixture.

The chemical analysis of a typical Class F fly ash is shown below along with that of cement. As can be seen, the fly ash is primarily silica and alumina with lesser amounts of iron and calcium. In addition there are small amount of sulfur, sodium, potassium and magnesium.

Chemical Analysis of Cement and Fly Ash

Oxide	Cement	Fly Ash
SiO2	21.3 %	49.0%
Al2O3	4.5	24.6
Fe2O3	4.0	7.3
MgO	2.4	1.6
CaO	63.1	9.1
Na2O	0.1	0.2
K2O	1.2	0.6
SO3	2.2	0.4

Specifications for fly ash are given in ASTM C 618, *Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete.* ASTM C 618 contains specifications for two classes of fly ash: Class F and Class C. Class F fly ash is produced from anthracitic and bituminous coals, it generally has a low-calcium content (less than 10% CaO) and up to 5% carbon. Class C "high-calcium" fly ash is produced from lignitic and subbituminous coals, it is typically 10 to 30% CaO and less than 2% carbon.

Both fly ashes are usually 60-85% glassy material, 10-30% crystalline compounds and some amount of carbon. The carbon is generally present as cellular particles larger than 45 μm, it is considered undesirable to have more than 5% carbon since it tends to increase the water requirement of the cement. Carbon contents are controlled indirectly by limiting the loss on ignition of the material. Loss on ignition is a standard test for all cements and mineral admixtures, it is typically done in conjunction with the compound analysis. Specifications are given in ASTM C114, *Standard Test Methods for Chemical Analysis of Hydraulic Cement.*

Most fly ash particles are solid spheres of glass but there may be a small number of hollow spheres, either cenospheres (which are completely empty) or plerospheres (which contain smaller spheres). The composition and properties of fly ash can vary considerably, in particular its specific gravity varies between 2.2 and 2.8, depending on the amount of these hollow spheres. The particles vary from $1 \mu m$ to $100 \mu m$ in diameter, more then 50% are under $20 \mu m$. The Blaine fineness of most fly ashes is between 300 and 500 m^2/kg.

Class F fly ash evolves considerably less heat than cement as it hydrates, it liberates the heat more slowly. Fly ash particles are approximately the same size as cement particles and the speed of the pozzolanic reaction is comparable to the hydration of C_2S. Thus adding fly ash has much the same effect as raising the C_2S content of the cement. Type I or II cement mixed with Class F fly ash can be substituted for Type IV cement in mass concrete. ASTM Class C fly ashes do not reduce the heat of hydration considerably. These cements have both cementitious and pozzolanic properties, many of them will hydrate and harden in less than 45 minutes when exposed to water [Komatsu and Panarese, 1990]. In the U.S., Class F fly ash is generally used at 20 -25 % by weight of the cement, Class C fly ash is sometimes used at higher rates.

Although the effects of fly ash have been studied extensively its behavior is still not well understood. It was originally thought that workability improved when part of the cement was replaced with fly ash because the fly ash particles acted like ball bearings and reduced the interference between aggregate particles. (Air borne materials like fly ash tend to be smooth and spherical whereas ground material like cement are typically solid, angular particles). Subsequent investigation has shown that the effect of fly ash is much more complex, it is actually believed to act somewhat like chemical water reducers [Helmuth, 1987]. The particle size distribution, morphology and surface characteristics of the fly ash appear to affect both the workability and the rate of strength development of the concrete.

11.3 Slag

Ground granulated blast furnace slag forms when molten blast-furnace slag is cooled rapidly either in water or water and air. If it is cooled quickly enough, most of the lime, silica and alumina are held in a noncrystalline (glassy) state. Depending on how it is cooled, the slag solidifies as either pellets or sand size particles; these are then ground to produce particles less than 45 μm. The reactivity of the slag will depend on the particle size, and the amount and composition of the glass. The thermal history is significant, in particular glass chilled from a higher temp and at a faster rate will be more disordered and thus more reactive. Slag particles smaller than 10 μm will contribute to strength at less than 28 days whereas particles between 10 and 45 μm contribute to later strength. As with cement itself, particles greater than 45 μm are difficult to hydrate.

When quenched in water rather than air and water, the slag contains more glassy material. It is also self-cementing, i.e. it does not require CH to form a cementitious product. If it hydrates by itself however, the amount of cementitious products formed and the rates of formation are insufficient for a structural material. When mixed with Portland cement, the hydration of slag is accelerated by the CH produced during the hydration of the cement. In addition some of the CH is consumed by the slag hydration, as a result the slag reaction is similar to that of the pozzolanic reaction. Slag typically has a Blaine fineness of approximately 500 m^2/kg. It is similar to high calcium fly ash in its mineralogic character and reactivity, both are primarily non crystalline and the reactivity of their high calcium glassy phase is on the same order. Slag is typically added to concrete at about 40% by weight of the cement. Although slag cements with greater than 70% slag are produced, they are typically used in patching materials or masonry mortars, they do not develop enough strength to be used in structural concrete.

11.4 Silica Fume

Silica fume, also referred to as microsilica, consists of glassy, spherical particles which are typically between 85 and 95% silicon dioxide (SiO_2). As opposed to fly ash and granulated blast furnace slag, which are typically used to reduce the cost of the concrete, silica fume is used primarily to improve its properties. During the past several years, the benefits of using silica fume in concrete have become widely recognized, consequently demand has increased and prices have risen greatly, it currently costs more than five times as much as cement. (Cement, in bulk is currently about four cents a pound, silica fume can be anywhere from twenty-five to forty-five cents a pound). The silica fume used in concrete is a by-product of the silicon and ferrosilicon manufacturing processes, it is produced when quartz is reduced with coal in electric arc furnaces. A silica based gas is emitted during production of the metal, the vapor cools rapidly as it rises and condenses to form the silica fume which is then collected in a bag house. Although very high purity microsilica is synthesized for use in the food industry, the cost, approximately two dollars per pound, makes it impractical for use in concrete.

Silica fume particles are on the order of .15 μm in diameter, i.e. about 100 times smaller than cement particles. It is typically used at the rate of 10 to 20% by weight of the cement; due to the difference in particle sizes, a 10% silica fume content means there will be approximately 50,000 silica fume particles for each particle of cement [Grace, 1990]. Its relative density is 2.2 and its specific surface, as measured by nitrogen adsorption is the range of 20 to 25 m^2/g. In comparison, cement has a relative density of 3.15 and a specific surface of approximately .35 m^2/g. (Tobacco smoke has a specific surface of about 10 m^2/g). A chemical analysis of a typical silica fume, compared to cement, is shown on the next page.

Chemical Analysis of Cement and Silica Fume [Grace, 1989]

Oxide	Cement	Silica Fume
SiO_2	21.3 %	85-95%
Al_2O_3	4.5	.5
Fe_2O_3	4.0	2.1
MgO	2.4	.3
CaO	63.1	.8
Na_2O	0.1	0.1
K_2O	1.2	1.0
SO_3	2.2	0.2

Silica fume is available in several forms:

- un-densified powder (bulk density approx 200 kg/m^3)
- densified powder (bulk density approx 500 kg/m^3)
- micropelletised (bulk density approx 700 kg/m^3)
- premixed with water as a slurry of approximately 50% solids

Because of its extreme fineness, silica fume may present handling problems, using it in the slurry or densified (air compacted) form alleviates these problems somewhat. The form in which it is used has a strong influence on the mixing procedures necessary to disperse the particles. The undensified form is actually seldom used since it takes up a considerable amount of space and thus causes transportation and storage problems as well as handling and mixing problems.

Since its very high specific surface results in a greatly increased water demand, a water reducing agent is typically required any time silica fume is used. Without a water reducing agent, attractive forces between the silica fume particles create a very cohesive, sticky mix.; distribution and deflocculation of the particles is difficult and intensive pre-mixing may be required. Normally superplasticizers rather than water reducers are used; the slurry form is sometimes pre-dosed with a superplasticizer. Superplasticizers allow a very workable mix to be produced even when the water to cement plus silica, w/(c+s), ratio is below .3. (Dosage of the superplasticizer is typically based on the microsilica content rather than the cement content.)

11.4.1 Effect of Silica Fume

Silica fume has two effects on concrete, it acts as an ultrafine "filler" material and it is also a pozzolan. As a filler, it increases the overall surface area of the dry mix and acts as a buffer between cement and aggregate particles. It also fills the voids between cement particles which greatly reduces the size of the pores in the hardened paste. As a pozzolan, it reacts with calcium hydroxide to form C-S-H. Because of its extreme fineness (high specific surface) and high glass content, silica fume is much more reactive than fly ash and its effect are evident at an earlier age.

The addition of silica fume typically causes a significant increase in compressive strength. The strength increase is partly due to the pozzolanic reaction since C-S-H contributes considerably more than calcium hydroxide to the strength of the concrete. In addition, by reducing the tendency for bleeding and segregation, silica fume increases the strength of the transition zone. Flexural strength is increased but to a lesser extent than compressive strength. The increase is due, in part, to the increase in strength of the transition zone, in addition the voids in both the bulk paste and the transition zone are smaller and therefore less effective as stress concentrators.

Since the greatly reduced pore sizes restrict the movement of water, both drying shrinkage and creep are reduced. The permeability of the concrete is also reduced which means there is an increased resistance to chemical (i.e. sulfates) attack. Due to the increased strength of the transition zone there may also be an increase in the elastic modulus [Grace,1990].

The main drawbacks to using silica fume is that it is expensive. It costs approximately 30 cents per pound (depending on what form it is in) and is generally added at the rate of 50-70 pounds/cubic yard of concrete. In addition it usually means that superplasticizers will be necessary which will add an additional five dollars per cubic yard. In many applications however, the increased material cost is more than offset by the increased rate and decreased cost of placement. Silica fume can be beneficial in pumping since the higher cohesion generates a more stable mix (i.e. one that is likely to travel through the lines as a plug). In addition, since there tends to be a better coating on the aggregate, friction on the lines and the pump is reduced.

11.5 Use of Mineral Admixtures

In general, when mineral admixtures are used, the water to cementitious materials w/(c+cm) ratio rather than the w/c ratio is stated, i.e. a concrete with 100 pounds water, 300 pounds cement and 100 silica fume would have a w/(c+cm) ratio of .25. This is sometimes also written simply as a w/cm ratio.

With fresh concretes that show a tendency to bleed or segregate, incorporating finely dissolved particles tends to improve workability by reducing the size and volume of voids and increasing the cohesion. This is particularly important when concrete is placed by pumping, fly ash is often used in pumped mixes when the aggregate is deficient in fines. In general, concretes made with fly ash and silica fume show less segregation and bleeding than plain concretes. Some slags however tend to cause a slight increase in bleeding, the reasons for this behavior are not well understood [Komatsu and Panarese, 1990]. Although concretes containing fly ash or ground slag usually require less water for a given workability than concretes containing only Portland cement, some fly ashes and slags will increase the water demand [Komatsu and Panarese, 1990].

11.6 Setting and Strength Development

Mineral admixtures can be used as a partial replacement for the cement, for the fine aggregate or a combination of the two. When used as a replacement for cement, fly ash and slags may retard the setting time of the concrete considerably; final set appears to be more affected than initial set [Gelber, 1986]. Concretes containing Class C ash generally develop strength faster than concretes with Class F ash, some studies has found that when used in small amounts Class C ash and some slags will exceed the strength of the plain concrete in 1 to 28 days [Komatsu and Panarese, 1990]. Other studies have found concretes containing slag and Type C have lower strengths at 1 and 3 days but substantially increased strength after about 7 days [Mehta and Monteiro, 1993]. Most Type F ashes show lower strengths at 28 days but higher ultimate strengths. Silica fume may show increased strength gain as early as 1 day, the greatest contribution to strength occurs between 3 and 28 days however [Komatsu and Panarese, 1990].

Temperature may play a factor in the strength development of mixes with mineral admixtures. It has been stated that the strength development of concrete with fly ash or ground slag is similar to normal concrete when cured around 70 F [Komatsu and Panarese, 1990]. No study was given as evidence of this claim however.

When mineral admixtures as used as a partial replacement for cement, the differences in specific gravities may require an adjustment in the mix design. As an example, fly ash typically has a specific gravity of about 2.5 versus 3.2 for cement. An equal weight replacement will result in a larger volume of fly ash and consequently a larger volume of paste. When used as a replacement for fine aggregate this is less of an issue since the specific gravity of most aggregate is about 2.65.

When used as a replacement for fine aggregate, all mineral admixtures tend to increase the strength of concrete at both early and late ages. The strength gain at early ages is in part due to a slight acceleration of the Portland cement hydration, perhaps because as the admixtures start to dissolve, they increase the amount of ions in solution. At later ages, the gain, which can be substantial, is due mostly to the pore size refinement and replacement of CH with C-S-H which result from the pozzolanic reaction.

11.7 Heat of Hydration

Fly ash and ground slag tend to reduce the amount of heat build up in concrete both because their heat of hydration is lower and because they hydrate slower. The effect of silica fume varies however depending on the w/c ratio of the concrete and the amount of silica added. It may also depend on the amount and type of superplasticizer used since this will affect how well dispersed the silica is, thus how available it is for hydration. One of the issues with adding silica fume appears to be whether all of the silica fume can, in fact, hydrate. When silica fume is used in very low w/c concretes, much of it may not hydrate, therefore the overall heat of hydration for the concrete will be lower [Smeplass and Maage]. Even if it does not hydrate the silica fume will still contribute to the strength of the concrete, simply because it reduces the amount of pore space.

Fly ash (particularly Class F) has been used quite successfully in massive structures (i.e. dams) to reduce problems with thermal cracking. Under normal circumstances, it does not react to any significant degree for several days, in addition, its heat of hydration is only about half that of cement. When fly ash is used as a replacement for cement, the temperature rise may be reduced almost in direct proportions to the amount of cement replaced [Komatsu and Panarese, 1990].

11.8 Durability

For the CTBM the primary concern regarding durability may be sulfate resistance. The fact that the pozzolanic reaction increases the resistance to sulfate attack may therefore be of value. Sulfate resistance is governed by the amount of reactive alumina in the cement paste as well as its permeability and CH content however. High calcium fly ash tends to contain highly reactive C_3A or C_4AS and is therefore less suitable than low calcium fly ashes for improving sulfate resistance. Slags also tend to contain reactive alumina but the sulfate resistance of slag cement will depend on both the the alumina content of the slag and the amount of slag. Slag with high alumina content will increase the susceptibility to sulfate attack when added in small amounts. Large amounts of CH are necessary for the formation of expansive ettringite however, cements with 60 -70 % or more slag contain so little CH that they are highly resistant to sulfate attack irrespective of the C_3A content of the Portland cement and the reactive alumina content of the slag. As noted above however, these cements are not sufficiently strong to be used as structural cements. Low (less than 11%) alumina slag will increase sulfate resistance even if used in small amounts, larger amounts of these slags are needed with higher C_3A cements.

11.9 Use of Mineral Admixtures in the CTBM

In general, there would seem to be little rational for using ground slag with the CTBM, it may however be worthwhile to investigate the use of fly ash and silica fume further. Both of these will increase the resistance to sulfate attack, the ultimate strength and the impermeability of the concrete. Silica fume in particular appears to have considerable promise since the w/(c+s) ratio of the concrete may be so low that it does not hydrate fully and therefore does not contribute greatly to the heat of hydration.

As has been discussed however, the effects of a mineral admixture can vary considerably. Before an admixture is accepted for use, it should be tested with the cement and aggregates being used to determine its suitability as far as water requirements, strength development, heat of hydration and durability. Testing must also be done to determine the optimum dosage and any possible effects of under or overdosage or improper mixing. Such testing is particularly critical in this case since the overall performance of the CTBM is extremely sensitive to the behavior of the concrete.

Chapter 12

Concrete Strength

The strength of hardened concrete is not its only important characteristic; depending on the application, its durability, volumetric stability and impermeability may be equally significant. It has become customary to assess concrete quality in terms of its compressive strength however; the general assumption is that an improvement in concrete strength will improve its other properties. Although this is often the case, there are many important exceptions. For example, an increase in cement content will increase the strength but it will also tend to increase the amount of shrinkage and creep. Concrete strength alone may thus be misleading in terms of choosing an appropriate mix design for a particular job. Furthermore, most concrete in practice is simultaneously subjected to a combination of compressive, shearing and tensile stresses in two or more directions. Uniaxial compression tests are the easiest to perform in a lab however; as a result the 28-day compressive strength determined by a standard uniaxial compression test is universally used as an indicator of concrete quality.

The principal source of strength in concrete is van der Waals forces. The small crystals of C-S-H, calcium sulfoaluminates and calcium aluminate hydrates possess enormous surface areas and adhesive capability. They adhere strongly to each other, in addition they adhere to the solids with low surface areas such as the CH, unhydrated cement grains and aggregate. Many of the properties of concrete (i.e. its elastic modulus, permeability and resistance to chemical attack) are in fact related to strength; they can be deduced with some degree of accuracy from strength testing.

12.1 Strength of Paste, Mortar and Concrete

The primary factor that governs the strength of a brittle material is its porosity. A number of models have been proposed to describe the basic strength-porosity relationship. For simple homogeneous materials it is often fairly well described by the expression:

$$S = S_O \, e^{-kp}$$

where S is the strength of the material at a given porosity p, S_O is the strength at zero porosity and k is a constant.

This equation and the many others that have been proposed represent a considerable simplification of the system however. The nature of the material, the size and shape of the pores and whether the pores are empty or full all have some effect, i.e. continuous pores reduce strength more than isolated pores. Nevertheless, even though the exact relationship between strength and porosity may not be clear, there is usually a strong relationship.

In 1947, Powers and Brownyard found that the 28-day compressive strength of Portland cement mortars is directly proportional to the gel/space ratio where they used the term gel/space ratio (X) to refer to the ratio of the solid products of hydration to the space available for these hydration products. Since the porosity will be equal to 1-X, the gel/space ratio is a representation of the capillary porosity of the paste in terms of measurable parameters.

When fully hydrated, 1 cm^3 of cement will occupy about 2.2 cm^3 of space. Before hydration begins, all of the space occupied by the mixing water is available for hydration products. After hydration has proceeded to a certain degree, part of this space will be filled with hydrated cement (the "gel"), the rest will be capillary pores. The gel/space ratio will depend on both the degree of hydration and the w/c ratio according to the relation:

$$X = .68\,\alpha\ /\ (.32\,\alpha + (w/c))$$

where alpha is the degree of hydration.

Powers and Brownyard found the relationship between the compressive strength (σ_c) and the gel/space ratio to be of the form:

$$\sigma_c = A\,X^n$$

where A is a constant representing the intrinsic strength of the cement gel (i.e. the strength at zero capillary porosity) and n is a constant having values in the range 2.6 to 3.0 depending on the cement.

For the mortars they tested Powers and Brownyard found the intrinsic strength to be 235 MPa (34,000 psi). As a result, this equation is often seen written as:

$$\sigma_c = 235\,X^3 \qquad \text{MPa}$$

$$\sigma_c = 34{,}000\,X^3 \qquad \text{psi}$$

The expression is independent of the mix design (w/c ratio), age or type of cement. It should be noted however that this is based on strengths obtained from 2-in mortar cubes. Tests on cement paste or on specimens of different geometries would presumably lead to different values of the constants. Powers and Brownyard in fact found that there was some dependence on cement composition, cements with higher C_3A contents (particularly above 7% C_3A) had lower strengths at a given gel/space.

When considering strength-porosity relationships, the gel porosity is included as part of the solid C-S-H, typically the gel porosity is fairly constant at about 26% by volume of the paste. The fact that the C-S-H (the major component of the paste) is itself a very porous solid accounts for the relatively low intrinsic strength of the paste

(235 MPA / 34 ksi). The gel porosity does therefore reduce the concrete strength, it does not do so to the same degree as larger pores however, in particular stress concentrations and rupture occur at large capillary voids and microcracks, not at the gel pores. (It should be noted at the same time however that large pores appear be more effective in relieving stress concentrations at crack tips.)

The above relationships are for mortar which is cement paste and fine aggregate, i.e. no coarse aggregate. Whereas in hardened cement paste or mortar the porosity can be related to strength, with concrete the situation is not as simple. The presence of microcracks in the transition zone between the coarse aggregate and the matrix makes concrete too complex a material for prediction of strength by precise strength-porosity relations. The general validity of the relationship probably holds however because the porosity of the component phases becomes strength limiting. With normal weight aggregate, the strength of the concrete will be governed by both the matrix and the transition zone. Typically, at early ages the transition zone is more porous, thus weaker; due to continuing chemical reactions with the aggregate, it may eventually become stronger than the bulk paste.

12.2 W/C Ratio

Even though the strength of concrete is largely dependent on the capillary porosity, this is not an easy quantity to measure, therefore it is not suitable for use in the mix design procedures. At any degree of hydration, the capillary porosity of a properly compacted concrete is determined by the w/c ratio however, consequently strength can be specified in terms of the w/c ratio. This relation was established in 1919 by Duff Abrams and is the basis for what is known as the Abrams law w/c ratio law:

$$\sigma_c = \frac{\mathrm{A}}{\mathrm{B}^{1.5(w/c)}}$$

where σ_c is the compressive strength at some fixed age and A is an empirical constant, usually taken to be 14,000 psi. B is a constant that depends on the cement and is usually taken to be about 4. Even though the Abrams w/c ratio law is not a physical law it is a very useful tool. It does not however give any consideration to the degree of hydration, the air content or the effects of the aggregate. In addition, although it applies fairly well to ordinary, workable structural concrete with aggregate up to 40 mm, it may not apply to mixes in which the maximum aggregate size or aggregate amount is very different from "ordinary" concrete such as mortars or mass concrete. Furthermore, at very low w/c ratio where full compaction is difficult to achieve, there may be large voids; Abrams' law will typically not hold for these concretes unless superplasticizers are used to facilitate compaction.

One problem with using the w/c ratio specified in the mix design as an indication of strength is that the w/c ratio of the concrete as placed may be different. Normally, in practice, a slump test is used to evaluate the concrete. Although a high slump typically indicates a high w/c ratio, there is no direct relationship between the slump and the w/c ratio. Thus there is no way to really tell whether there is additional water in the mix, either from the aggregate or due to additions at the site.

12.3 Effect of Aggregate

Although the w/c ratio is the most important factor affecting strength, the properties of the aggregate cannot be ignored. The aggregate parameters that are most important are the shape, texture, maximum size, grading (particle size distribution) and mineralogy. The aggregate strength itself is of less importance since aggregate is generally much stronger than the matrix and transition zone, except in the case of lightweight aggregate or high strength concrete.

The aggregate texture depends on whether the aggregate is a naturally occurring gravel which tends to smooth or crushed rocks which tends to be rough and angular. Surface texture affects both the bond and the stress level at which microcracking begins but tends to have little effect on the ultimate compressive strength. Surface texture does affect the tensile strength however, consequently the ratio between the tensile and compressive strength depends to some degree on the aggregate. Concrete containing rough-textured or crushed aggregate will show somewhat higher strength (especially tensile strength) at early ages because of the stronger mechanical bond between the aggregate and the hydrating paste. At later ages, when chemical interaction begins to take effect, the influence of the surface texture will be reduced. In addition somewhat more mixing water is usually needed to obtain a given workability with rough textured aggregate, thus the advantage due to better physical bonding may be lost.

Larger maximum aggregate size affects the strength in several ways. Because the use of larger particles reduces the specific surface area (area per unit weight) of the aggregate, the area for bonding is also less; this tends to reduce the concrete strength. In addition, larger aggregate tends to result in weaker transition zones containing more microcracks, larger aggregate also provides more restraint on volume changes in the paste and thus may induce additional stresses which tend to weaken the concrete. However, concrete with larger aggregate requires less paste to achieve a given workability, thus for a given amount of cement, there can be a lower w/c ratio. The net effect of aggregate size will vary with the w/c ratio of the concrete. At low w/c ratios the porosity of the transition zone plays an important role in strength, low w/c ratio concretes will show a greater decrease in strength as the size of the aggregate increases. Transition zone characteristics affect tensile strength more than compressive strength; tensile strength decreases proportionately more with increasing aggregate size, thus the tensile/compressive strength ratio tends to decrease with increasing aggregate size. Concretes made with larger aggregates also tend to exhibit more strength variability, probably due to some tendency toward segregation.

The differences mentioned here with respect to size and surface texture are typically not very large however. In addition, the indicated trends only hold for a given type of aggregate; the effects may be obscured by the use of a different type of aggregate. Differences in the mineralogical composition of the aggregate may affect strength, in particular, substitution of limestone for sandstone may have a significant effect on long term (i.e. 56 day) strength [Mehta and Monteiro, 1993].

In the range of aggregate contents normally used, the exact volume of aggregate is only of secondary importance in determining concrete strength. In general, at a constant w/c ratio, a higher strength can be achieved by using a leaner (higher aggregate content / less paste) mix. This is probably because the lower paste content means less total porosity. If a constant workability is maintained, the strength of concrete dependent on the cement content. This is consistent with Abrams law since the workability is primarily a function of the amount of paste, increasing the amount of cement for a given amount of paste means you have decreased the w/c ratio. (The amount of paste is equal to the amount of cement plus the amount of water.)

12.4 Effect of Cement

The strength of cement comes primarily from the hydration of the C_3S (early strength) and the C_2S (later strength). Thus the relative amounts of these compounds will influence the rate of strength development. The influence of the cement composition is usually limited to early ages however. Although cements with different compositions may show considerable differences in strength development up to about 1 month, at later ages the differences become less significant. At ordinary temperatures, the degree of hydration after 90 days is usually similar for the different types of Portland cement, including blended cements (those which include pozzolans) [Mehta and Monteiro, 1993]. In general, cements that hydrate more slowly, whether through changes in composition, curing conditions or the use of admixtures tend to hydrate more fully and thus develop higher ultimate strengths.

The rate of hydration and strength gain increases with increasing fineness of the cement. Typically the maximum cement particle size is about 50 μm, about 10 to 15% are less than 5 μm and perhaps 3% are less than 1 μm. The fraction of particles less than 3 μm in diameter has the greatest influence on 1-day strengths while the 28-day strengths are most affected by the 3 to 30 μm fraction. Particles with diameters greater than about 75 μm may never hydrate fully and so contribute proportionately less to strength.

It should be noted that cements of a given type vary considerably from plant to plant, even within a given plant the cement characteristics will vary over time due to changes in raw materials, burning conditions, etc. It has been estimated that this variability in cement quality leads to a coefficient of variation in concrete strengths on the order of 5% [Mindess and Young, 1981].

12.5 Effect of Admixtures

The ability of mineral admixtures to react at normal temperatures with the calcium hydroxide in the paste and form additional calcium silicate hydrate can lead to a significant reduction in porosity of both the matrix and the transition zone. Consequently, considerable improvements in ultimate strength and watertightness can be achieved. Mineral admixtures are especially effective in increasing the tensile strength of concrete due to their improvement of the matrix-aggregate bond.

Chemical admixtures may have very little effect on the ultimate strength except insofar as they affect the w/c ratio or the porosity of the concrete. Admixtures have their greatest effect on the rate of strength gain, either by accelerating or retarding the hydration of the cement. A decrease in the rate of strength gain of concrete will generally lead to somewhat higher ultimate strengths.

12.6 Rate of Strength Development

The rate at which concrete develops strength depends on the rate of hydration and the initial w/c ratio. The rate of hydration depends primarily on the cement and the curing conditions. For a given cement low w/c ratio concretes will gain strength more rapidly than high w/c ratio mixes since their initial porosity is lower.

Even though concrete continues to gain strength almost indefinitely, the 28-day compressive strength is typically used as a criterion of acceptance. It is useful to look at how strengths at different times is related to the 28 day strength however. High performance (i.e. high early and high ultimate strength) concretes are being used more and more; for many of these applications the 28 day strength is not really meaningful. In practice, it is common to do both 7 and 28 day compressive tests. Although it varies with cement type, admixtures and curing temperature, the ratio of 28 to 7 day strength is usually between 1.3 and 1.7 and generally less than 1.5. The British Code of Practice CP114 allows a 7-day strength equal to at least two thirds of the 28-day design strength to be used for acceptance tests. In addition, it permits the strength beyond 28 days to be considered if the structure is to be loaded at a later age.

12.7 Tensile Strength

It is generally assumed that the factors that affect compressive strength will affect other types of strength (tensile, flexural, shear) in the same way. Although this tends to be true, there are no simple, unique relationships between the different strengths. The tensile strength of concrete is much lower than the compressive strength, largely because cracks can propagate much more easily under tensile loads. In particular, when concrete is under compression, a significant amount of energy is needed to form and extend cracks in the matrix, when it is under uniaxial tension, considerably less energy is needed. Tensile failure is due to the rapid propagation and linkage of cracks, both preexisting cracks in the transition zone and newly formed cracks in the matrix.

Although tensile strengths are usually not considered directly in design, they are can be important since cracking is due to tensile failure. The relationship between tensile and compressive strengths is not a simple one, it depends on the age and strength of the concrete, the type of curing, the type of aggregate, the amount of air entrainment and the degree of compaction. In addition, it depends on how the tensile strength is measured: whether by direct tension, splitting or flexure. In general, as the age or strength level increases, the ratio of tensile to compressive strength (σ_t/σ_c) decreases. Since crushed coarse aggregate seems to improve tensile strength more than compressive strength, the ratio also depends to some degree on the type of aggregate. As compared to moist curing, air curing reduces the tensile strength more than the compressive strength, probably because of the effect of drying shrinkage cracks. Incomplete compaction and air entrainment affect the compressive strength more than the tensile strength however.

In general the ratio of the direct tensile strength to the compressive strength ranges from about .07 to .11. Since splitting tension (σ_{st}) values tend to be slightly higher than direct tension, the σ_{st}/σ_c ratios are also slightly higher, they are typically between .08 and .14. Due to problems with determining the results accurately, direct tension tests are seldom done. Flexural tests are the most common way of estimating tensile strengths, they give results that are substantially higher than direct tension tests; the ratio of flexural to compressive strength (σ_f/σ_c) ranges from about .11 to .23. Although a number of formulas have been developed to relate the tensile strength to the compressive strength, they are all, at best, approximations. The equation used by ACI is:

$$\sigma_f = .62\ (\sigma_c)^{1/2}\ \text{MPA}$$

$$= 7.5\ (\sigma_c)^{1/2}\ \text{psi}$$

The Committee European du Beton (CEB) however relates the axial tensile strength to the characteristic (design) compressive strength according to the equation:

$$\sigma_t = .3\ (\sigma_c)^{2/3} \quad \text{MPa}$$

with a range of variability of ± 30% . Alternatively, they suggest that σ_t can be taken to be equal to 60% of σ_{st}.

12.8 Shear Strength

Pure shear is not often encountered in concrete structures, nevertheless failure of concrete quite often occurs from a combination of shear and normal stresses. Although a knowledge of the shear strength, τ, of concrete would be useful, it has not been possible to measure it directly. The normal "pure shear" test, torsion of a hollow cylinder, produces a principal tensile stress equal to the shear stress but acting at 45 degrees to it. Since concrete is stronger in shear then in tension, it fails in tension rather than shear.

In an attempt to estimate shear strength, tests have been done on very short span beams with loads applied very close to the supports. In some tests, τ has been found to be only slightly larger than the tensile strengths, in other tests it has been found to be 50 to 90% of the compressive strength. This could be due to the fact that either tensile or compressive stresses may be acting at the same time. A more reliable estimate of shear strength can be obtained from combined stress tests. When plotted on a Mohr failure diagram, the shear strength, τ_o, is represented by the point at which the failure envelope intersects the vertical axis. When determined by this method, the shear strength of concrete is approximately 20% of the compressive strength.

12.9 Impact Strength

Even more than the other mechanical properties of concrete, the impact strength appears to depend on the method of testing. Although a lot of research has been done, there are no standard tests and there is still no agreement on the relationship, if any, between impact strength and other strengths. Some researchers have found no correlation, others have found it varies as .5 to .75 of the cube compressive strength. Still others have suggested that it is more closely related to tensile strength. Curing conditions appear to be important; the impact strength of dry concrete is less than continuously moist-cured concretes, this is probably due to shrinkage cracks that develop when concrete is dried.

When the impact strength is determined by the number of blows that the concrete can withstand until there is no rebound of the impacting hammer, the type of aggregate seems to have an effect. Thus, the nature of the cement-aggregate bond may be more significant than for other types of strength.

12.10 Multi-Axial Stress

In addition to voids of various size and shape in the bulk paste concrete contains microcracks in the transition zone, consequently the failure modes are complex. Various experimental investigations have indicated that compressive failure in concrete is governed by the strength of the matrix, whereas tensile failure is governed by the aggregate-matrix bond. In practice however, concrete is rarely subjected to only a single type of stress. In the general case, it might be subjected to a combination of compressive, tensile and shearing stresses all acting simultaneously. The behavior of concrete under these combined stresses is still not completely understood. There are no generally accepted standard tests for concrete subjected to multi-axial stresses, furthermore there is no generally accepted criterion of failure.

In general compressive strength is increased by a transverse compressive (confining) stress and decreased by a transverse tensile stress. The increase in compressive strength when a lateral confining pressure is applied can be very large, in addition there can be a large increase in strain at failure. The effects of a confining pressure depend to some degree on the details of the concrete mix however, they tend to be more significant for weak concretes. For a given w/c ratio, the strength usually increases more for concretes with a high aggregate content, the strength increase is smaller for cement pastes that it is for concrete. Strength in biaxial tension seems to be about the same as in uniaxial tension however tensile strength is reduced by subsequently applied transverse compressive stresses. This reduction is greater for concrete with a high w/c ratio, it is also greater for concrete than for cement paste.

Most of the empirical relationships that have been developed for triaxial strength ignore σ_2, the intermediate principal stress. In general, σ_2 does not have a significant influence on behavior under triaxial loading. However since concrete has different Mohr failure envelopes for biaxial and triaxial compression, the effect of σ_2 cannot be ignored completely. The effects of multiaxial stresses are actually quite complicated; in addition to the type of loading, the stress history must be considered; failure is determined not only the by the ultimate stresses but also by the rate of loading and the order in which the stresses were applied.

12.11 High Strength Concrete

There are essentially two methods to get high early strength with concrete. One is to use some kind of accelerated curing, i.e. high-pressure steam curing such as is used in the precast industry. The other is to use concrete with a very high cement content and a very low w/c ratio, similar to what is done in the production of high strength concrete. Since steam curing is not a practical alternative in a tunnel environment, the CTBM will probably need to use a very high cement, low w/c ratio concrete. As a result, the concrete will also have a high ultimate strength. It is thus useful to have an understanding of the behavior and properties of high strength concrete.

One difference between high strength and high early strength concrete is that high strength concrete is not usually made with a rapid-hardening (e.g. Type III) cement. Type I and II cements are actually preferable since they produce slightly higher ultimate strengths. In the production of high strength concrete (or any "high performance" concrete) however, uniformity of cement performance is as important as the potential strength gain, if not more so. A cement which consistently produces a slightly lower strength concrete is better than one whose performance is erratic or overly sensitive to such factors as temperature and humidity.

High strength concrete may show somewhat higher strengths as early as one day by virtue of their very low initial porosity. As discussed previously, the single most important factor affecting the strength of concrete is its porosity. Although this is controlled primarily by the w/c ratio of the paste, the paste must have adequate workability (i.e. it must be possible to compact it fully). At low w/c ratios concrete is extremely difficult to mix, place and consolidate unless a superplasticizer is used; in other words although a low w/c ratio has a positive effect on porosity since it reduces the amount of water in the mix, this may be counteracted by the fact that the mix cannot be fully compacted.

Crushed stone is typically used in high strength concrete because its rough surface texture creates a better bond than gravel and it has a greater surface to volume ratio, thus increasing the area for bonding. It is important to ensure that the aggregate surfaces are clean however; clay and silt will tend to weaken the aggregate-paste bond. To increase the total surface still more and thereby improve the total bond contribution, the maximum aggregate size is usually 19 mm (3/4 in).

This small aggregate size means that a high volume of paste is needed to provide sufficient workability. The combination of low w/c ratio and high paste volume means that cement contents will be quite high, generally in the range of 400 to 600 kg/m^3 (650 to 1000 lb/yd^3). It has been found however that with increasing amounts of cement, a strength plateau is eventually reached, i.e. there is no further increase in strength with increasing cement Mehta and Monteiro, 1993]. It is thought that this is due both to the inherent inhomogeneity of the paste and the fact that the large crystals of calcium hydroxide represent weak areas of cleavage under stress. Such inhomogeneous and weak areas in the transition zone are especially vulnerable to microcracking because of thermal or drying shrinkage. One way to reduce inhomogeneities is to use pozzolans since the processes of grain and pore size reduction produce a more uniform system. In addition, as discussed in Chapter 11, pozzolans reduce the overall amount of calcium hydroxide by transforming it into a product that is similar to the hydration product of the C_3S.

Pozzolans (either fly ash and silica fume) are used in almost all high strength concrete because of their strengthening effect on the aggregate-paste bond. In general, they tend to cause a decrease in early strength however. For this reason, specifications for high strength concrete are often based on the 56 or 98 day strength rather than the 28 day strength.

In most high strength concretes, the failure surface passes through both aggregate and paste, in some cases, the quality of the aggregate may be the principal limitation to achieving high strength. Studies at Cornell on concrete with compressive strength ranging from 30 to 75 MPa (4,500 to 11,000 psi) determined that high strength concrete behaves more like a homogeneous material than normal strength concrete. The elastic modulus is higher and more linear because of a decrease in the amount of microcracking in the transition zone. Because of this decrease in progressive microcracking, high strength concretes show a more brittle failure mode and less volumetric dilation. Creep in high strength concrete is much less than in normal strength concrete in addition the amount of microcracking associated with shrinkage, short-term loading and sustained loading is significantly less [Carrasquillo, 1981].

In low and medium strength concrete made with normal aggregate, both the transition zone and the matrix have an effect on strength and there is a direct relation between the w/c ratio and strength. However with high-strength concrete (concrete with a w/c ratio under 0.3) there are disproportionately large increases in the compressive strength with very small reductions in the w/c ratio. This phenomena is attributed mainly to a significant improvement in the strength of the transition zone at very low w/c ratios. One of the explanations is that the size of calcium hydroxide crystals become smaller with decreasing w/c ratios [Mehta and Monteiro, 1993]

There is some feeling that when very low w/c pastes are used, the gel/space ratio relationship developed by Powers should be modified [Mindess and Young, 1981]. The intrinsic strength at "zero porosity" was estimated by extrapolation of data in well hydrated pastes with w/c ratios between .4 and .7. The intrinsic strength thus reflected the strength of a paste with a certain minimum intrinsic porosity. In pastes at very low w/c ratios, complete hydration cannot occur and the intrinsic strength may be higher due to a contribution from the remnants of unhydrated cement present. It is not known whether any work actually has been done on this.

Chapter 13

Elastic Modulus

The static modulus of elasticity for a material under tension or compression is given by the slope of its stress-strain curve. Although cement paste and aggregate, the two components of concrete, are essentially elastic, concrete itself is inelastic, particularly at higher stresses. Plastic (irreversible) deformation occurs after even very short periods of load and as a result the stress-strain curve is highly non-linear.

There are two reasons for this; the first is that the modulus of elasticity of aggregate is substantially higher than that of the paste. Under an applied stress, the strain in the paste will tend to be considerably higher than that in the aggregate. The response of the concrete to applied load will depend on the cement-aggregate bond, if the bond is weak there may be considerable plastic deformation in the paste. The aggregate will deform less however and thus provide a restraining influence, as a result the overall response of the concrete will be highly non-linear. The modulus of elasticity of light weight aggregate is close to that of paste, thus concretes made with light weight aggregate tend to show more linear stress-strain behavior. Similarly, high strength concretes of necessity have a strong bond, thus their stress-strain curves tend to be more linear.

The second reason for this inelastic, non-linear behavior is the microcracks in the transition zone. There will always be cracks and flaws in concrete, even before it is subjected to load. Most of these cracks are bond cracks at the cement-aggregate interface, they are in part the result of the differences between the elastic moduli of

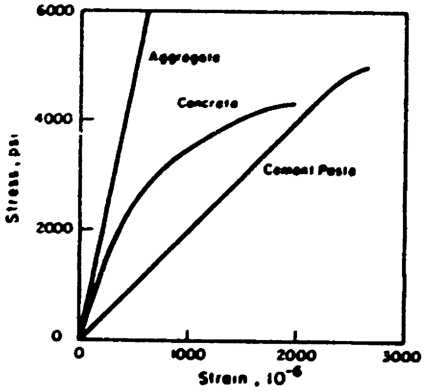


Figure 4-2 Typical stress-strain behaviors of cement paste, aggregate, and concrete. (Based on T. C. Hsu, ACI Monograph 6, 1971, p. 100.)

The properties of complex composite materials need not be equal to the sum of the properties of the components. Thus both hydrated cement paste and aggregates show linear elastic properties, whereas concrete does not.

Figure 13-1: Typical Stress Strain Behavior [Mehta and Monteiro, 1993]

the paste and the aggregate, they are also of their different coefficients of thermal expansion and their different responses to changes in moisture content. The difference in moduli may lead to considerable stress concentrations if there are differential volume changes due to continued hydration, temperature differentials or drying of the concrete. Since the bond strength is less than the strength of the matrix, at least at early ages, the interfacial region is typically the "weak link" in the material. thus cracks will tend to form in this region.

As with other brittle materials, the fracture process in concrete passes through three states: crack initiation, slow growth, then rapid growth leading to failure. These three states determine the stress-strain and failure behavior of concrete. Below about 30% of its ultimate compressive strength, concrete is fairly elastic. Although bond cracks already exist at low stresses they are quite stable and have little tendency to propagate. In addition to these preexisting cracks, there is probably some additional crack initiation where strain concentrations are large. These cracks are also stable at low loads but their formation probably accounts for the slight nonlinearity of the stress-strain curve even at low stresses.

Between about 30 and 50% of the ultimate stress, the cracks begin to propagate slowly. Most of the crack growth is in the interfacial region, the system of bond

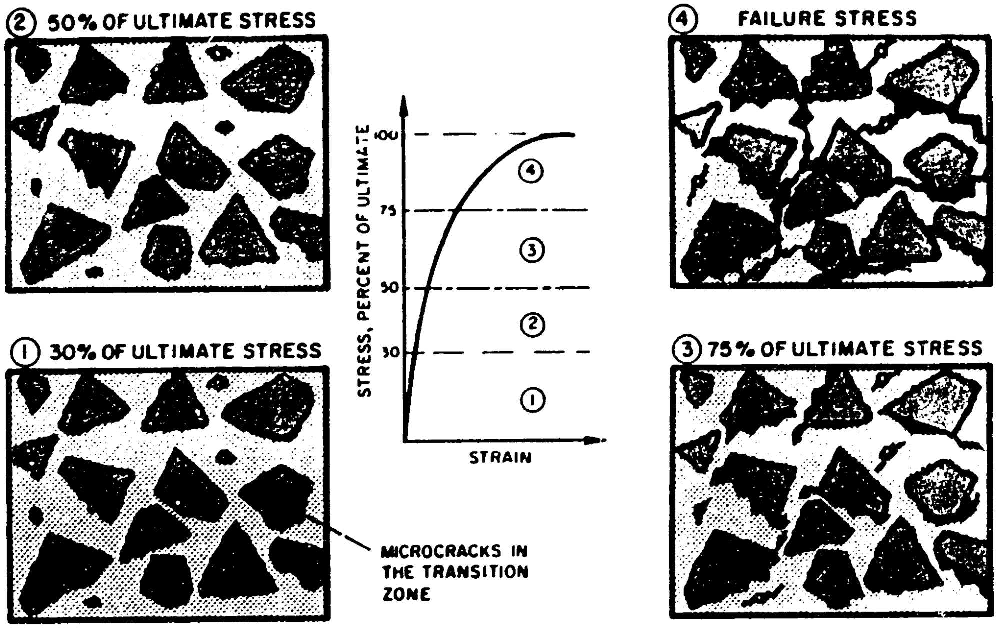


Figure 4–3 Diagrammatic representation of the stress-strain behavior of concrete under uniaxial compression. (Based on J. Glucklich, *Proc. Int. Conf. on the Structure of Concrete*, Cement and Concrete Association, Wexham Springs, Slough, U.K., 1968, pp. 176–85.)

The progress of internal microcracking in concrete goes through various stages, which depend on the level of applied stress.

Figure 13-2: Stages of Failure in Concrete [Mehta and Monteiro, 1993]

cracks multiplies and grows in a stable manner and the stress-strain curve begins to shown increasing curvature. At this point there is still very little cracking in the matrix, however once the stress exceeds about 50% of ultimate, the cracks begin to extend into the matrix. A much more extensive and continuous crack system begins to develop as the matrix cracks begin to connect the originally isolated bond cracks. Beyond about 75% of the ultimate stress rapid crack growth occurs in the matrix, the crack system eventually becomes unstable and failure occurs.

The non-linearity of the stress-strain curve may have particular significance for the design of the tunnel lining. When loaded at stresses approaching its ultimate compressive strength, concrete has a very low modulus, consequently there will be large deformations. In the case of the tunnel lining, large deformations may mean that a significant portion of the ground's own strength can be mobilized and thus less load is applied to the tunnel. It will probably be necessary to perform an iteration to establish actual loads and deformations, in order for this to be meaningful however, it will be necessary to have a fairly good understanding of what the stresses in the vicinity of the tunnel lining are. It will also be necessary to determine acceptable values for deformation, this will depend to some degree on what type of tunnel it is.

One of the most important variables, but probably the hardest to model accurately will be the impact of time on the entire stress-deformation process. As it hardens, both the compressive strength and the elastic modulus of the concrete increase, at the same time, the applied loads are changing due to the advance of the CTBM. To get an accurate portrayal of the tunnel, it will be necessary to use appropriate values for both the material properties and the loads at each time step.

13.1 Determining the Elastic Modulus

Since the stress-strain curve for concrete is non-linear even at small strains the modulus of elasticity can vary, depending on how it is calculated. There are three common methods of calculation giving rise to three moduli: tangent, secant and chord.

1. The tangent modulus is the slope of the tangent line at any point on the curve, its value will depend on the point at which it is calculated. The initial tangent modulus is the slope of the tangent to the curve at the origin and is the closest approximation to a truly elastic modulus. It is of little practical value however since it only applies to very small stresses and strains.

2. The secant modulus is the slope of line from the origin to the point on the stress-strain curve which corresponds to 40% of the failure load.

3. The chord modulus is the slope of the line from an initial offset of 50 microstrains (50 μ-in/in) to the point corresponding to 40% of the failure load. The offset corrects for a slight concavity that is often observed at the start of a stress-strain curve. This concavity is thought to be caused by preexisting cracks closing up under the applied load.

The chord modulus is easier to determine experimentally than the initial tangent modulus, it is also smaller which, for most applications, is conservative. It underestimates the incremental strain that occurs when an additional stress is imposed on a loaded system however. The tangent modulus at the appropriate load is a better measure of the response to relatively small additional stresses.

Procedures for calculating the chord modulus are given in ASTM C469, *Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression*. Depending on the type of aggregate and the compressive strength of the concrete, values range from 14 to 41 GPa (1 to 10 x 10^6 psi). Typically however, the modulus of elasticity is not determined by testing but is estimated from empirical relationships between the modulus and compressive strength. The relationship given in the ACI 318 is:

$$\mathrm{E_C} = .043\ \rho^{3/2}\ (\sigma_c)^{1/2}\ \mathrm{MPa}$$

$$\mathrm{E_C} = 33\ \rho^{3/2}\ (\sigma_c)^{1/2}\ \mathrm{psi}$$

where E_c is the secant modulus, ρ is the unit weight of the concrete and σ_c the compressive strength of a standard 150 x 300 mm (6 x 12 in) cylinder in MPa (psi). For normal weight concrete with a typical density of 2320 kg/m^3 (145 lb/ft^3), this reduces to:

$$\mathrm{E_C} = 4{,}730\ (\sigma_c)^{1/2}\ \mathrm{GPA}$$

$$\mathrm{E_C} = 57{,}000\ (\sigma_c)^{1/2}\ \mathrm{psi}$$

For normal weight concrete the CEB (Committee European du Beton) Model Code (1990) uses the formula:

$$\mathrm{E_C} = 2.15 \times 10^{4} (\sigma_{cm}/10)^{1/3}\ \mathrm{GPa}$$

where σ_{cm} is the average 28 day compressive strength. These values are stated to be accurate to ± 30%. The ACI and CEB values are for quartzitic aggregate, they should nominally be adjusted if another type of aggregate is used. Given that the expression is only an approximation, it is not clear that adjusting for the aggregate is completely necessary however the factors given are as follows:

Basalt, dense limestone	1.2
Limestone	0.9
Sandstone	0.7

The CEB expression is considered valid for design strengths up to 80 MPa (11,600 psi) while the ACI expression is valid up to 41 MPa (6000 psi). For concrete with a compressive strength above 6,000 psi, ACI recommends using the formula:

$$E_c = 0.06\sqrt{f'_c} + (1 \times 10^{6}) \text{ psi}$$

13.2 Dynamic Modulus

The dynamic modulus of elasticity is the modulus corresponding to a very small, instantaneous strain; it is thus approximately equal to the initial tangent modulus. The standard method for measuring the dynamic modulus is to vibrate a concrete specimen at its natural frequency according to the procedures given in ASTM C215, *Test Method for Fundamental Transverse, Longitudinal and Torsional Frequencies of Concrete Specimens.* The dynamic modulus is calculated according to the following formula:

$$E_d = K\ W\ m^2$$

where W is the weight of the specimen, m is the fundamental frequency and K which is a constant which depends on the type of the vibration (transverse or longitudinal) and the specimen dimensions and shape. The dynamic shear modulus, G_d, is given as:

$$G_d = B\ W\ m^2$$

ASTM C215 gives formulas for calculating both K and B according to the specimen geometry.

The dynamic modulus is typically about 20 percent higher than the static modulus for high strength concrete, 30 percent higher for medium strength concrete and 40 percent higher for low strength concrete. The dynamic modulus is primarily used for analyzing structures subject to earthquake and impact loading. In addition it is useful as a non-destructive measure of the stiffness of the concrete, it can be used to monitor progressive changes in the material due to chemical attack or freeze-thaw damage.

13.3 Factors Affecting the Elastic Modulus

In homogeneous materials there is generally a direct relationship between density and modulus of elasticity. In heterogeneous, multiphase materials such as concrete however, the modulus of elasticity depends on the volume fraction and elastic modulus of the major constituents. Furthermore, in concrete the characteristics of the transition zone are important. The relationship between the strength and elastic modulus arises from the fact that both are affected by the porosity of the constituent phase. Many of the factors that affect strength will affect the elastic modulus, although not necessarily to the same degree.

Among the coarse aggregate characteristics that affect the elastic modulus of concrete, density seems to be the most important. Dense aggregate has a higher elastic modulus and thus a greater ability to restrain matrix strains, this in turn results in concrete with a higher modulus. The elastic modulus of aggregate with low porosity such as granite, trap rock and basalt is in the range of 10 to 20 x 10^6 psi, sandstones and limestone range from 3 to 7 x 10^6 psi. Lightweight aggregates are somewhat lower, depending on their porosity their elastic modulus may be as low as 1 x 10^6 psi or as high as 4 x 10^6 psi. Generally the modulus of lightweight of lightweight concrete ranges from 2 to 3 x 10^6 psi which is between 50 and 75 percent of the modulus for the same strength normal-weight concrete. Other aggregate properties may have a minor effect on the modulus of elasticity of the concrete. The surface texture, maximum size, shape, grading and mineralogical composition can affect microcracking in the transition zone and thus influence the stress-strain curve.

The elastic moduli of the paste phase (the matrix and transition zone) is also determined primarily by its porosity. The porosity of the matrix depends on the w/c ratio and air content as well as the degree of hydration. The porosity of the transition zone also depends on the w/c ratio and degree of hydration, in addition the bleeding characteristics of the mix, the degree of consolidation, and potential chemical interaction with the aggregate can be important. The porosity of both the matrix and the transition zone can be significantly reduced by the use of pozzolans, the elastic modulus is consequently increased. Typical values for the elastic modulus are in the range of 1 to 4 x 10^6 (the same as lightweight aggregate).

At early ages, the porosity of the transition zone can be significantly higher than the matrix due to both a higher void density and the presence of microcracks, as a result its modulus can be significantly lower. With time there is a densification of the transition zone due to chemical reactions between the cement paste and aggregate. This appears to affect the modulus more than the compressive strength however, at later ages, i.e. 3 months to 1 year, the elastic modulus increases at a greater rate than the compressive strength [Mehta and Monteiro, 1993].

In addition, drying appears to affect the matrix and transition zone differently. Regardless of the mix proportions or curing age, concrete specimens which are dry when tested show about 15 percent lower elastic modulus than the corresponding specimen tested in a wet condition. Compressive strength is about 15 percent higher however when the specimens are dry when tested. It is thought that drying causes the matrix to gain strength due to an increase in van der Waals forces, but causes the transition zone to lose strength due to microcracking. If the matrix is strength determining, the compressive strength of the concrete will increase on drying even though the modulus decreases. Another possible factor is that if the adsorbed water in the C-S-H is load-bearing, its presence will contribute to the elastic modulus but the disjoining pressure will reduce the van der Waals forces, thus lowering the strength

[Mehta and Monteiro, 1993].

13.4 Shear Modulus

The shear modulus (modulus of rigidity, G) which determines the behavior under shear stresses is not easy to determine by stress-strain measurements. It is best determined from the resonant frequency of torsional vibration according to ASTM C 215.

13.5 Poisson's Ratio

For a material subjected to simple axial load, the ratio of the lateral strain to axial strain within the elastic range is called Poisson's ratio (ν). Although it is not generally used in concrete design it is needed for analysis of statically indeterminate structures such as tunnel linings. For saturated concrete, Poisson's ratio is in the range of 0.2 to 0.3, however for dry concrete it is generally between .15 and .20 and once it has dried the change is not completely reversible. It can either be determined by direct strain measurements in uniaxial compression (ASTM C469) or it can be calculated from the equation:

$$\nu = E_d \,/\, 2G_d - 1$$

where E_d and G_d are the dynamic elastic and shear moduli determined according to ASTM C 215.

Poisson's ratio is usually somewhat higher (typically around 0.24) when determined dynamically rather than by direct strain measurements; this is probably more representative of elastic behavior. Although there appears to be no consistent relationship between Poisson's ratio and the w/c ratio, age or aggregate gradation, the value is generally lower in high-strength concrete.

Chapter 14

Volume Changes in Concrete

Concrete changes slightly in volume for a number of reasons; an understanding of these changes is helpful when designing and analyzing concrete structures, particulary indeterminate structures like tunnel linings. Volume changes can be caused by chemical effects such as carbonation shrinkage, sulfate attack and the disruptive expansion of alkali-aggregate reactions. Typically however, volume changes are the result of expansion and contraction due to changes in temperature and moisture content. In addition, there will be elastic, and possibly plastic, deformation due to applied load. The primary significance of these deformations, whatever their cause, is whether their interaction will result in cracking. In the case of a tunnel lining where some cracking is probably unavoidable, the issue is whether the amount of cracking is unacceptable.

For the sake of convenience, volume changes are expressed in linear rather than volumetric units. They are often expressed in millionths or percentages, i.e. 600 millionths (approximately 3/4" per 100 ft.) could be expressed as either .000600 or .06%. Ordinarily the volume changes that occur in concrete are small, ranging in length change from about 10 millionths up to about 1000 millionths [Komatsu and Panarese, 1990]. If concrete were free of restraint, these normal volume changes would be of little consequence. In service however, most concrete is restrained to some degree and as a result, significant stresses can develop. Tensile stresses in particular are a problem since they are what will cause cracking. In the case of the

CTBM, the tunnel environment is such that drying shrinkage is not likely to be a problem. As determined by finite element analysis [Bobet, 1994], the applied stress will be primarily compressive. There may be significant tensile stress due to thermal shrinkage however. High stresses and cracking can be prevented or minimized by controlling the variables that affect volume changes.

14.1 Thermal Expansion

As with most solids, concrete expands slightly as its temperature rises and contracts as its temperature falls. The strains associated with temperature change depend on both the coefficient of thermal expansion of the material and the magnitude of the temperature rise or drop. The coefficient of thermal expansion,α, is the change in unit length per degree of temperature change. In the case of concrete, the coefficient of thermal expansion is essentially a function of the aggregate since the the aggregate normally makes up about 75% by volume of the concrete. Other factors which may have an effect are the cement content, w/c ratio, temperature range, concrete age and relative humidity. Experimental values of the coefficient of thermal expansion for concrete made with different types of aggregates are shown below:

Coefficient of Expansion of Concrete Made with Different Types of Aggregate (Millionths per °F)

Quartz	6.6
Sandstone	6.5
Granite	5.3
Basalt	4.8
Limestone	3.8

These values, especially those for granites and limestones may vary widely however [Komatsu and Panarese, 1990]. If there is no test data for a particular concrete, the coefficient of thermal expansion is usually taken to be 5.5×10^{-6} /°F (5.5 millionths).

For a concrete subjected to a rise or fall of 100 F, this amounts to a length change of 2/3" in 100 feet (550 millionths).

In most concrete structures, there will not be such extreme temperature changes so thermal shrinkage is not usually a major concern. However, in structures where there is relatively poor heat dissipation or where there is a high cement content, the heat of hydration may cause the concrete temperature to rise considerably within the first few days. The initial temperature rise will cause expansion of the concrete and although expansion under restraint usually produces a compressive stress, the elastic modulus of the concrete at this point is fairly low. Consequently, the compressive stresses will be low and in design it is usually (conservatively) assumed that there is no initial compressive stress. Subsequent cooling to ambient temperature will cause shrinkage strains however; depending on the elastic modulus, the degree of restraint and the stress relaxation due to creep, the tensile stresses may be large enough to cause cracking.

14.2 Shrinkage and Cracking

As noted previously, if a concrete element were free to move there would be no stress associated with the thermal deformation on cooling. In practice however, the concrete will be restrained externally by the subgrade and connecting members (in the case of a tunnel liner, by the ground surrounding the liner). It will also be restrained internally by reinforcement and differential deformations due to temperature gradients within the concrete. As a very simple example:

> If the coefficient of thermal expansion α of the concrete is 5 x 10^{-6}/°C, and the temperature rise is 50 °C, the thermal strain caused by the subsequent temperature drop will be $\alpha * \Delta T$ or 250 x 10^{-6}. The elastic modulus,E, of ordinary concrete can be approximated as 3 x 10^{6} psi. If the concrete member was completely restrained and there was no creep, the resulting tensile stress would be:
>
> $$\sigma_t = (E * \epsilon) = 3 \text{ x } 10^6 \text{ psi} * 250 \text{ x } 10^{-6} = 750 \text{ psi.}$$

Since the tensile strength of most concrete is less than 750 psi, this is likely to cause cracking. In most structures however, there will be some stress relaxation due to creep, in addition there will not be complete restraint. The degree of restraint, K_r, at any particular point in the concrete will be a function of the elastic modulus at that point versus the elastic modulus of the restraining element. For a rigid foundation, i.e. concrete on rock, there will be full restraint at the interface ($K_r = 1.0$) but as the distance from the interface increases, the restraint will decrease. This phenomenon is partly responsible for the "curling" of slabs on grade. The concrete at the bottom of the slab is restrained by the subgrade and is not free to move. The concrete at the top of the slab, however, is restrained by the (relatively low modulus) concrete underneath it and is thus able to shrink considerably. ACI-207.2R gives formulas and tables for calculating K_r as a function of depth versus length of an element. In addition it gives formulas for calculating K_r for a nonrigid foundations where K_r at the interface is less than 1.0. In the case of a tunnel lining however the geometry of the structure is significant, it is probably more appropriate to determine the degree of restraint via a finite element analysis.

14.2.1 Creep

Creep in concrete is typically defined as a time dependent deformation that begins immediately on load but continues, at a decreasing rate, as long as the concrete remains loaded. The amount of creep which will take place will depend primarily on the magnitude of the stress, the age and strength of the concrete when the stress is applied, the length of time the concrete is loaded. It can also be affected by a number of other factors including the type, amount and maximum size of the aggregate, the type of cement, size, shape and volume to surface ratio of the element, ambient temperature, relative humidity and admixtures. A complete discussion of creep prediction is beyond the scope of this work, particularly since there is considerable disagreement over what mathematical approaches are appropriate for representing different aspects of the phenomena. With respect to cracking in the tunnel liner, the restrained thermal shrinkage will cause an tensile strain. As a result of the corresponding applied stress, the concrete will tend to creep (extend slightly), thus reducing the tensile strain and consequently the tensile stress. Both ACI (ACI Committee 209) and CEB have developed simple, empirical methods for calculating creep coefficients, these coefficients are typically used in practice. Creep coefficients are given in terms of both creep at a given time (C_t) and ultimate creep (C_{ult}). When concrete is drying under load at 40 % RH, C_{ult} will be in the range 1.30 to 4.15, ACI recommends a value of 2.35 if experimental data is not available.

A calculation of the shrinkage stress, accounting for creep and degree of restraint is shown below:

$$\sigma_t = K_r \ (E \ / \ 1+\phi) \ (\alpha * \Delta T)$$

where: σ_t = the tensile stress

K_r = degree of restraint

E = elastic modulus

α = coefficient of thermal expansion

ΔT = the temperature change

ϕ = the creep coefficient of concrete

14.3 Temperature Rise in Concrete

With small concrete elements, temperature rise is usually not a problem since the generated heat can be dissipated rapidly. In thicker members however there is potential for considerable heat buildup since heat is dissipated at a rate inversely proportional to the square of the least dimension. As an example, a 6 inch thick wall cooling equally from both sides might take approximate 1 1/2 hours to dissipate 95% of its developed heat. A five foot thick wall would take an entire week to dissipate the same amount of heat [Komatsu and Panarese, 1990].

If the temperature rise due to heat of hydration were adiabatic (no heat was being lost to the environment), the magnitude of the temperature rise would be primarily a function of the amount and composition of the cement. Cements high in C_3A and C_3S will generate more heat per gram than cements high in C_2S, thus they will cause a greater temperature rise. Although the fineness of the cement and the placing temperature affect the rate at which heat is generated they do not affect the amount of heat generated. A finer cement will hydrate more rapidly and a given cement will hydrate more rapidly at higher temperatures, nevertheless, in both cases the total heat generated will be similar.

In practice, the temperate rise in concrete is not adiabatic, the magnitude of the temperature rise will thus depend on the rate at which the heat is being generated versus the rate at which it is being dissipated. As noted above, the rate at which heat is dissipated will depend on the geometry of the element. In addition it will depend on the thermal diffusivity of the concrete and the environment at the surface of the concrete as measured by the surface transmission coefficients.

Thermal diffusivity is an indication of how fast heat will move through a substance, heat moves faster through a substance with high thermal diffusivity. Thermal diffusivity, κ, is defined as:

$$\kappa = \mathrm{K}/\mathrm{c}\rho \quad \mathrm{m}^2/\mathrm{hr}$$

where: K = the conductivity of the concrete, J/m.h.K (Btu/ft.h.F)
c= the specific heat of the concrete, J/kg.K (Btu/lb.F)
ρ = the density of the concrete, kg/m^3 (lb/ft^3)

The thermal conductivity of a material is the heat flux transmitted through a unit area under a unit temperature gradient. The thermal conductivity of concrete depends on the aggregate type and the moisture content, density and temperature of the concrete. Typical values of thermal conductivity vary from 14 Btu in./hr.$ft^{2\circ}$F (1.9 W/m.k) for basalt to 24 Btu in./hr. $ft^{2\circ}$F (3.5 W/m.k) for quartzite.

The specific heat of a material is the quantity of heat needed to raise the temperature of a unit mass of the material by one degree. The specific heat of concrete is typically in the range of .22 to .25 Btu/lb °F. Since neither the specific heat nor the density vary significantly for normal-weight concrete, the thermal diffusivity is a function of the conductivity. Thermal diffusivity for concretes vary from .032 ft^2/hr

(.0030 m^2/hr) for concrete made with basalt to .058 ft^2/hr (.0054 m^2/hr) for concrete made with quartzite.

Surface transmission coefficients indicate how rapidly heat will flow across an interface. Coefficients for concrete in different environments are shown on the next page.

Environment	Surface Transmission Coefficient (kcal/m^2.h.C)
Concrete-curing water	300.0
Concrete-air	11.6
Concrete-metal-air	11.6
Concrete-wood-air	2.6
Concrete-insulation-air	2.0

As can be seen, wooden forms (concrete-wood-air) will prevent heat loss, almost to the same extent as if the concrete was insulated. Steel forms do not really prevent heat loss (the surface transmission coefficient is the same as air) however they will absorb some of this heat. As a result the temperature at the concrete-form interface is significantly higher than if the concrete were exposed to air. In slightly simplified terms what happens is that, instead of there being a temperature differential in the concrete, the temperature differential is in the steel. The concrete temperature will be fairly constant, the inside face of the form will be at the temperature of the concrete and the outside face will be at the ambient temperature. When the forms are removed the concrete will be exposed to a sudden, potentially very large temperature differential.

14.4 Cracking as a Function of Temperature Drop

In theory a large enough temperature drop ΔT will crack concrete regardless of its age or strength, provided the concrete is fully restrained. A rough approximation of the tendency for cracking can be done quite easily and is probably easiest to visualize with respect to pavement.

If a long section of concrete pavement is cast without joints, the aggregate in the concrete and thus the concrete overall will expand slightly due to the heat of hydration. Although it will tend to shorten as its temperature drops, it will be prevented from doing so by subgrade friction. Since the ACI-318 approximation for the modulus of elasticity is 57,000 $\sqrt{f'_c}$, the tensile stresses that develop will be proportional to the square root of the compressive strength. The tensile strength is also proportional to the square root of the compressive strength however (using the common approximation $f_t = 7.5\ \sqrt{f'_c}$). As the tensile strength of the concrete increases, so does the elastic modulus and consequently the stress for a given thermal strain. As an example of these calculations:

> Assume that the coefficient of thermal expansion of the concrete, α is 5.5 x 10 $^{-6}$/°F. If restrained against contraction at both ends, the tensile stress in the concrete is: $f_t = \alpha * E$. If it is approximated according to ACI- 318, $E = 3.12 * 10^6$ when $f'_c = 3000$ psi.

The tensile stress σ_t is thus $\alpha * E =$

$$5.5 * 10^{-6} * 3.12 * 10^{6} = 17.2 \text{ psi /°F} .$$

If the tensile strength is approximated as 7.5 $\sqrt{f'_c}$, $f_t = 410$ psi when $f'_c = 3000$ psi. Thus, in theory, the temperature drop, ΔT, necessary to crack the concrete is:

$$410/17.2 = 24 \text{ °F}$$

The general equation for ΔT is:

$$\Delta T = \frac{f_t}{E * \alpha}$$

$$= \frac{7.5\sqrt{f'_c}}{57{,}000\sqrt{f'_c} * \alpha} = 1/7600\ \alpha$$

When $\alpha = 5.5 * 10^{-6}$ therefore, $\Delta T = 24$°F for any age or strength concrete.

The equations shown above actually represent a considerable simplification. In particular, neither the tensile strength nor the elastic modulus of concrete are really proportional to the square root of the compressive strength, particularly at early ages. Although an enormous amount of experimentation has been done in an attempt to find more appropriate relationships, the general feeling seems to be that as of yet, nothing better has been found.

14.4.1 Temperature Control in Massive Structures

In mass structures such as dams, the concrete is usually of relatively low compressive strength and potentially low quality. To avoid cracks in these concretes it is recommended that the internal temperature not be allowed to rise more than 20 to 25 °F over the mean ambient temperature. In these structures, temperature rise can be controlled through the use of a low cement content, large aggregate size, high coarse aggregate content and cooling the concrete with embedded chilled water pipes. Since most of these strategies considerably reduce the early strength of the concrete they are not particularly applicable for the CTBM. Other strategies used in massive structures include precooling the materials (particularly the water) and using a pozzolan such as fly ash, the heat of hydration of a pozzolan is 25 to 50% that of cement (depending on the pozzolan), they also tend to hydrate slower than cement. Both of these strategies will reduce early strength but the effect can tailored by altering the quantities. As noted in chapter 13, using a pozzolan also tends to produce a higher quality concrete.

14.4.2 Temperature Control for the CTBM

In the case of the CTBM, the important issue is to prevent excessive temperature differentials between the interior concrete and the surface concrete once the slipform moves ahead. If the temperature differential is kept low, the concrete will be able to cool slowly to ambient temperature with little or no surface cracking. With most cements, the rate of hydration is greatest during the first three days, consequently, the rate of heat evolution will also be greatest during this time. However as the interior of the concrete is increasing in temperature, the surface concrete may be cooling and contracting, if the temperature differential becomes too great, there will be cracking. The width and depth of the cracks will depend on the temperature gradient between the hotter internal concrete and the cooler concrete surface.

A rule of thumb based primarily on field experience is that the maximum temperature differential between the interior and exterior of these higher strength concretes should not exceed about 36 °F. This will prevent surface cracking, it will also reduce microcracking in the transition zone around large aggregate. Some feel that the differential for concrete made with granite and limestone (which have low thermal coefficients) can be higher. It is generally recommended, however, that the differential be kept to less than 36 °F unless tests on the actual mix indicate a higher differential will not cause problems [Komatsu and Panarese, 1990]. In some applications, the concrete is insulated to prevent temperature differentials, some type of insulating mechanism may be necessary for the CTBM if it is to achieve the proposed advance rates.

Chapter 15

Shotcrete Use in Tunneling

Shotcrete is being increasingly used in tunnel construction as part of both temporary and permanent linings. Consequently, it is useful to compare shotcrete technology and requirements with those of the CTBM. One of the main problems with shotcrete, particularly in overhead work is rebound of the aggregate. When sprayed concrete (shotcrete) is applied to a hard surface, only the mortar fraction is able to adhere initially. As subsequent layers are applied and the thickness of wet concrete increases, it forms a soft substrate for large aggregate to bed into, thus rebound is reduced. In order to create a soft surface, the mix should be kept as wet as possible without reaching the point of slumping, no layer should set until the subsequent layer has been placed, inner layers should then set rapidly to support the weight of the outer layers [Dransfield, 1988].

15.1 Shotcrete Accelerators

Accelerators can be used to increase the rate at which the cement hydrates; since the hydration products produce a very adhesive substrate the amount of rebound is reduced. The British Concrete Society specifications for accelerators are typical; they require an accelerator to produce initial set in less than 3 minutes and final set in less than 12 minutes. They also require an 8 hour strength of 4 MPa (560 psi) and a 24 hour strength of 10 MPa (1450 psi) for shotcrete containing an accelerator.

Ultimate compressive strength is often a secondary requirement for shotcrete however, particularly if it is being used as an initial lining.

The main active ingredients in most shotcrete accelerators are sodium silicates and aluminates. Aluminates are used in both powder and liquid form, normally at dosage rates of between 2 and 5% by weight of the cement. At high dosage rates, hydration is rapid and the ASTM final set value (penetration resistance of 27.5 MPa) is quickly exceeded. Silicates are normally only used as liquids and are less effective than aluminates, much higher dosages are needed to achieve the same acceleration. Due to concerns with toxicity, there have been attempts to develop organic chemicals based on amines and selected hydroxylated compounds. Organics can produce a very fast set and are normally employed at about half the dosage rate of inorganic accelerators. In addition, they are less alkaline and therefore safer to use. They are significantly more expensive than the aluminate and silicate accelerators however and thus are not widely used at present.

The way in which accelerators affect set is not fully understood. The reaction is different if hydration starts before the addition of the accelerator i.e. if the cement is pre-wetted or premixed with damp aggregate prior to the addition of water. The reaction is also affected by the cement's chemical composition, i.e. it is harder to accelerate a sulfate resisting cement (i.e. one which has a low level of tricalcium aluminate), this implies that the reaction is at least, in part, associated with the tricalcium aluminate

In the case of the silicate and aluminate accelerators, acceleration is thought to be due to the precipitation of colloidal calcium silicate and aluminate. The accelerator reacts with calcium and hydroxide ions which come from the dissolution of cement particles, according to the equation shown below ($CaSiO_3$ is the colloidal calcium silicate precipitate):

$$Na_2SiO_3 + Ca^{2+} + 2(OH)^- \rightarrow CaSiO_3 + 2NaOH$$

The colloidal precipitate has several effects; it introduces a large amount of fine, precipitated material into the voids between cement grains and thus helps to fill and bridge the gaps. It also provides a large number of additional sites for nucleation of the hydration reactions. The very early cement hydration products can bind into the precipitate to produce a very fast initial set. The formation of the calcium silicate or aluminate also releases alkali metal hydroxides. Since these are more basic than calcium hydroxide they accelerate the dissolution of the silicates in cement. This results in a more rapid reaction of the tricalcium silicate phase and hence higher earlier strengths [Dransfield, 1988].

Other acceleration mechanisms have been proposed, however, in light of the fact that the accelerators are not as effective with sulfate-resisting cement or when prehydration of the cement has occurred. The tricalcium aluminate-gypsum reaction is the basis of one proposed mechanism. When it is by itself, tricalcium aluminate hydrates very rapidly. Since unrestrained hydration of tricalcium aluminate in commercial cement can give rise to a flash set; gypsum is interground with the cement clinker. During hydration, the tricalcium aluminate combines with gypsum to give ettringite which forms as a coating around the cement grain and slows down hydration. When soluble aluminates are used with Portland cement, they may upset this balance. The soluble aluminates can combine with the gypsum and prevent the formation of ettringite, thus allowing the tricalcium aluminate to set very quickly [Dransfield, 1988].

The rate at which the concrete sets is critical to its performance; in particular immediate (flash) set must be avoided. If the concrete sets before it hits the substrate or so quickly afterwards that subsequent layers do not have a soft surface to bed into, the rebound will remain high. Accelerators are therefore formulated to have a slight built-in set delay and then stiffen rapidly, overdosing an accelerator can increase the rebound problem if it causes setting to occur too quickly [Dransfield, 1988].

It should be noted that the accelerators used in shotcrete are primarily set accelerators as opposed to strength accelerators, thus they only increase the rate of strength development to a certain point. Once the rate of strength development slows, it does not increase again until about the time that a control mix without accelerator would start to stiffen. Accelerators are typically used only when necessary since they tend to reduce long term strength, they also add significantly to the material cost. In addition, since most of them are highly caustic, they require extra safety precautions for handling and placement.

15.2 Specifications and Reinforcing

Shotcrete is most often used with rock bolts or with lattice girders in rock which is too unstable for bolts. For structural use, it is typically reinforced with wire mesh, although steel (and sometimes polypropylene) fibers are becoming popular as an alternative. Steel fibers have been shown to significantly increase flexural strength and toughness, in addition they are usually cheaper and easier to use than wire mesh.

The total thickness of shotcrete used for temporary support is usually 2-6", depending on the ground conditions and the strength of the shotcrete. When it is used as part of the permanent structure, the thickness can increase to 8 - 12", the number of passes used to produce this thickness is typically left up to the contractor. Strength specifications will depend on the application, they are often specified for either 8 hours, 72 hours and 28 days or 4 hours, 24 hours and 28 days. Typical values might be 5-7 MPa (750-1000 psi) at 8 hours, 19-21 MPa (2800-3000 psi) at 72 hours and 28-42 MPa (4000-6000 psi) at 28 days. This is significantly different from the CTBM where target strength may be on the order of 25 MPa at 4 hours.

ACI 506 R-90 *Guide to Shotcrete* covers the general methodology of shotcreting, ACI 506.1-89 *State of the Art Report on Fiber Reinforced Shotcrete* and ASTM C1116 are specifics for fiber reinforced shotcrete. When steel fibers are used, toughness index requirements (I5, I10, I30) may be specified as per ASTM C 1018.

15.3 Silica Fume

Silica fume is sometimes used to increase the adhesion and cohesion of shotcrete, particularly in overhead work. The increased cohesion reduces rebound, allows shotcrete to be placed in thicker layers, and means the cement does not have to set as fast. Silica fume also has a beneficial effect on long term strength due to its action as both a pozzolan and an ultrafine filler. As a filler it reduces the porosity of the paste, thus increasing both strength and impermeability. As a pozzolan, it improves the mortar-aggregate bond. The densified powder form of silica fume is not recommended for shotcrete work because of problems with mixing, typically the slurry form is used.

Chapter 16

Concrete Pumping

Most well proportioned, dense concretes are pumpable as long as they are plastic, i.e. pliable and capable of being molded. Although concretes with slumps from 2 to 7 inches have been successfully pumped, a slump of about 4 inches is usually considered ideal. The key point in pumping is that the force of the pump must be transmitted through the continuous phase (the water) in order to move the discrete particles of aggregate and cement. The concrete mix must be dense enough to transmit the applied force without segregation but it should not have so many fines that there is high frictional resistance.

The performance of a mix when pumped will depend on the aggregate type, shape and grading as well as the cement and water content. The simplest way of looking at these variables is to consider the void content between the aggregate particles and the volume of cement paste required to fill these voids. Ideally all of the aggregate particles should be coated with paste; since coating the particles causes them to separate, the void volume is actually slightly greater than what is measured as the aggregate void volume. Thus, the volume of paste (cement, water, pozzolan) must exceed the volume of aggregate voids by a small amount (3-4%).

If the paste is not at least equal to the void volume, segregation failure may occur. Pressure exerted by the pump forces the water though empty voids and out of the mix, leaving an aggregate plug lodged in the pipe. Segregation failures can be eliminated by reducing the size and volume of the voids in the aggregates, in most cases, this is accomplished by including appropriate proportions of the finer sizes of the fine aggregate. A typical recommendation is that the fines content (cement plus material smaller than .2 mm) should be at least 350 kg/m^3 when the maximum aggregate size is 20 mm and 400 kg/m^3 when the maximum aggregate size is 10 mm.

16.1 Concrete Flow

With a properly formulated mix, pumped concrete flows through a pipeline in the form of a plug. The plug is separated from the pipe by a lubricating grout layer of water, cement and fine sand particles, the lubricating layer for concrete flowing in a 100 mm diameter line at 30 m^3 /hour is typically about 3 mm thick.

16.1.1 Saturated Flow

The concrete plug itself consists of aggregate, sand, and cement particles separated by a continuous water layer which is hydraulically linked to the water in the lubricating layer. The velocity is essentially constant across the plug, i.e. there is no relative velocity between the aggregate particles, the velocity drops rapidly across the lubricating layer and is zero at the pipe wall. The resistance to the flow of the concrete is a combination of hydraulic shearing of the lubricating layer and friction of the solid particles in contact with the pipe wall. The amount of frictional resistance depends on the state of the concrete, the frictional resistance of concrete which is in a saturated state (there is sufficient water to fill the voids of the dry materials, with some excess) is negligible compared to concrete which is in an unsaturated state.

To measure the pumpability of a concrete mix, two parameters should be measured:

1.) the permeability or dewatering characteristics
2.) the flow resistance

For the range of concretes and concreting materials that are typically pumped, flow resistance values do not require high pumping pressure. In addition, although in exceptional cases excessively high flow resistance may require high pumping pressures and thus a larger pump, this is something that could be determined from the outset, it is not likely to cause failure during pumping. Therefore, the emphasis has been on studying the dewatering characteristics of mixes rather than flow resistance. Browne and Bamforth (1977) however worked out the following relations for flow resistance.

16.1.2 Saturated Concrete

With a saturated concrete, the flow resistance consists of two separate components, an adhesion resistance which exists even when the concrete is stationary and a factor related to the velocity of flow in the pipeline. An equation for the flow resistance would therefore be something similar to the following:

$$R = A + KV^n$$

where: R is the flow resistance

A is the adhesion

V is the velocity of the flow

K and n are constants for a particular concrete and are related to the mix proportions and workability, they are higher for concretes with lower workability.

16.1.3 Unsaturated Flow

When concrete is pumped in an unsaturated (frictional) state, Browne and Bamforth proposed the following equation for the flow resistance:

$$R = A + \mu P_r$$

where: A = adhesion resistance

μ = coefficient of friction between the concrete and the pipe wall

P_r = the radial pressure in the concrete

The flow resistance is thus a function of P_r, the radial pressure in the concrete, rather than the velocity of flow. The radial pressure in unsaturated concrete will not be the same as the axial pressure however and the relationship between the axial and radial pressure varies with different pump pressures. The value of the adhesion, A, may be an order of magnitude higher for unsaturated concrete than for saturated concrete.

16.1.4 Pressure Distribution

In practice, it difficult to determine the values for A, K and n for saturated flow. As a result, the pressure distribution in a pipeline is usually given in terms of the flow resistance, R:

$$\Delta P = 4Rx/D$$

ΔP = change in pressure
R = flow resistance/unit area of pipe
D = internal pipe diameter
x = distance along the pipe

Typical values for R (referred to in pumping manuals as friction losses) are on the order of .05 psi / sq ft.

16.2 Admixtures

Variations in the concreting material account for the major proportion of pipeline blockages, thus there may be problems even with a well designed mix. The aggregate for example may vary considerably in grading, shape and water content, particulary if it stored or handled incorrectly. Admixtures can be used to some extent to minimize the effect of these on-site variations. In addition, they can be used to increase the range of mix designs which may be successfully pumped, reduce the risk of pipeline blockages and increase rates of placing concrete through small bore, e.g. 75 mm lines.

Low cement (< 300 kg/m^3) concrete is difficult to pump since without the use of admixtures. The grout flows through the void channels extremely rapidly, in particular the grout along the pipewall is forced out, leaving a nest of aggregate that forms a blockage. Water thickening materials increase the viscosity of the water, some also cause the cement particles to flocculate, thus providing a further thickening effect. Among the chemical used as thickeners are polyethylene oxides, cellulose ethers and alginates. Very low concentration can produce significant increases in the water, and therefore the grout viscosity. There are many grades of each chemical so a wide range of viscosity characteristics is possible. Water thickeners are only available as powders however and there are no cheap, reliable dispensers to disperse very small quantities of powders into mixers. Because of handling difficulties therefore, it is more common to use air-entraining admixtures to faciliate placement of these mixes [Hewlett, 1988].

Concretes with a cement content of between 300 and 350 kg per cubic meter of concrete are preferred for pump mixes, these concretes usually has optimum water flow characteristics. High cement content (> 350 kg/m^3) concretes tend to have stiff cement pastes that do not have the required lubrication characteristics. The high surface area of the mix constituents coupled with a low w/c ratio produces a grout layer which exhibits very high friction. Since this layer does not allow the central plug of concrete to move down the pipeline easily, low pumping speeds and blockages may result. Water reducing agents and superplasticizers are often used to release extra mixing water to the cement grout and thus reduce the grout viscosity.

Typically, the use of admixtures for pumping is not something that can be rationalized on an economic basis, it is more that by using admixtures, a wider range of cement contents and aggregates can be used. When specifying admixtures, one must asses the various parameters which affect the pumping process, e.g there is little value in using a plasticizer when the mix shows dewatering characteristics. The concrete for the CTBM will almost certainly have a high cement content, thus the problem will be how tc avoid high pipeline friction. To achieve adequate flow characteristics a superplasticizer rather than a water reducer will likely be necessary.

16.3 Pumpability Tests

Although a number of methods of testing concrete for pumpability have been developed, none have been standardized by ASTM. Obviously, the rate at which water can permeate through a mix is significant; Browne and Bamforth proposed a method for measuring this which they called the Pressure Bleed Test. In this test, a small quantity of mix is placed in a pressure pot and the amount of bleed water which comes through a filter membrane is measured. This test can also be used to investigate the performance of admixtures, especially those of the water-thickening type.

Parker et al (1977) proposed using the vane shear test as a tentative index of pumpability. Using a steel fiber reinforced concrete made with a regulated set cement, they found the threshold of pumpability to be when the pumping resistance was about 4kPa (.6 psi), this corresponded to about a 75 mm (3 in.) slump. Obviously the required vane shear values will depend on the pump size, pipe size and mix characteristics. Nevertheless, if a criterion was established for a given pump and pipeline, the vane shear test could be used to assess pumpability over a fairly wide range of mix designs.

16.4 Pumping Specifications

The gradations and relative proportions of the fine and coarse aggregate are important factors in pumpable concrete mixes. The objective is to produce a mix which has both a small amount of voids and a high resistance to segregation. ACI 304 recommends that the fine aggregate conform to the ASTM C33 grading curves, in particular it recommends a smooth gradation without a deficiency or excess of any particular size. The most important factor is that there be enough of the finer sizes, i.e. material retained on the No. 100 (150 μm) and No. 200 (75 μm) sieves. [Cooke, 1990]. With very high cement content concretes, the amount of these fractions is usually reduced however . Although the gradation of the coarse aggregate is not as crucial, a smooth gradation curve results in a denser mixes. Coarse aggregate should preferably be rounded or cubical to minimize the amount of surface area per volume. The ratio of fine to coarse aggregates for minimum voids varies with the maximum aggregate size but usually is about 50%.

Although steel pipe is typically used when pumping concrete there is sometimes a flexible rubber hose attached at the discharge end to facilitate placement. The frictional resistance of the rubber hose is approximately three times greater than that of steel pipe, consequently these hoses should only be used in short lengths. The minimum recommended line size for conventional (non fiber reinforced) concrete mixes is normally on the order of 3 to 4 times the maximum aggregate size. Pipelines with an inside diameter of 4 and 6 inch are most common and since the diameter of the discharge end of some pumps is as large as 8 inches, a reducer may be needed to channel the concrete into the pipeline. A reducer will require the concrete to undergo a severe reworking; as a general rule, the entire pipeline system should be chosen so that minimum reworking is required and resistance to the flow of the concrete is as low as possible. General recommendations for pumping are given by ACI Committee 304, in the publication "Recommended Practice for Measuring, Mixing, Transporting and Placing Concrete".

Chapter 17

Conclusions

This work has attempted to provide a general overview of concrete as a construction material. It has also attempted to address the requirements of the CTBM. The overriding requirements of the CTBM, as currently proposed, is that the concrete have a high early strength and be pumpable. At the advance rates proposed in earlier works, the concrete will need to develop a strength on the order of 30 MPa at four hours. To achieve such a high strength, it will be necessary to use a concrete with a very high cement content and a very low w/c ratio. In order to make such a mix pumpable it will almost certainly be necessary to use a superplasticizer. A strength of 30 MPa may not be attainable with an ordinary Portland cement however, even a Type III (High Early) cement; it may thus be necessary to use a proprietary cement. Although there are a large number of high early strength and rapid setting cements available, most of them are marketed as patching products rather than structural cement. In particular, they tend to have very low tensile strengths. Only two cements, Pyrament from Lone Star Systems and Rapidset from CTS Cement Manufacturing Company, appear to have been tested in actual construction (a highway repair project).

High Early Strength

One of the major points stressed in this work is the difference between a cement which is rapid setting and a cement which has high early strength. Cements which are rapid setting (or admixtures which accelerate set) produce concrete which develops a small amount of strength very quickly. this type of behavior is useful in applications like underwater patching where the concrete must be able to resist wave action very quickly. It is also useful for shotcrete work in tunnels since the rapid set reduces the amount of rebound. The amount of strength developed however is far less than required for a tunnel lining that is supporting a ground load. In the case of the CTBM, the concrete will need to develop a significant amount of strength very quickly.

Most of the research in high early strength concrete has been done with respect to highway repairs. The loading is thus somewhat different than what is encountered in a tunnel lining. Although a pavement may be subjected to load at early age, the load is not likely to be continuous, thus creep is not a major concern. Creep however is likely to be an issue in a tunnel lining given that a fairly large load will be applied to the concrete at a very early age. In addition, concretes made with a chemical accelerator or a high-early strength cement are sometimes more susceptible to creep than ordinary Portland cement concrete. Some amount of creep may actually be desirable in a tunnel lining since deflection of the liner will cause the ground to mobilize a portion of its own strength and thus reduce the load on the lining. Excessive creep may cause problems with the intended function of the tunnel however. This is particularly true for transportation tunnels which may have overhead guide lines, vents or electrical conduits. The issue of creep was not really addressed in this work, future work should probably examine it in some detail.

Traditional concrete design makes a number of assumptions about the behavior of the concrete with regards not only to creep but also to such issues as shrinkage and moment distribution. As noted above, the concrete used in the CTBM will probably have a very low w/c ratio and a very high cement content, consequently, it will have a very high ultimate strength. The traditional assumptions used in tunnel design should be looked at carefully to determine whether they are appropriate for a high strength concrete and in addition whether they are appropriate when the concrete will be loaded at such at an early age.

Thermal Shrinkage

During the course of this work, it came to light that there might be a significant problem with thermal cracking in the tunnel lining. As cement hydrates, the heat of hydration causes the temperature of the concrete to rise. Subsequent cooling to ambient temperature can produce significant shrinkage strains and consequently large tensile stresses, if the stresses are large enough, cracking will occur. In particular, large stresses can occur if the cement at the interior of a concrete mass is still hydrating and thus rising in temperature but the surface of the concrete is cooling and thus contracting. A rule of thumb used in the concrete industry is that if there is more than a 30 degree temperature differential between the interior concrete and the surface concrete, cracking is likely to occur. In a tunnel lining, this cracking will tend to occur circumferentially, through the thickness of the lining. As shown by finite element modeling [Bobet, 1994] there is very little compressive stress in this direction (along the axis of the tunnel).

In discussions with the research staff at W.R. Grace Inc, it was learned that they had done a study on one of the tunnels constructed for the subway system in Los Angeles. This tunnel was to be jump-formed and the original plans were to remove the forms after fifteen hours. A finite element analysis of the heat flow and temperature distributions showed that this was likely to cause cracking however. A fairly in-depth analysis was done using different values for both the concrete temperature and the ambient tunnel temperature [Berke, 1994].

Fresh Concrete

Typically in concrete construction, it is the properties of the hardened concrete, particularly its strength, that are important. In the case of the CTBM however, the fresh concrete is an integral part of the machine's operation. Thus the properties and behavior of the fresh concrete are of considerable importance. The properties of fresh concrete as well as some of the methods of testing fresh concrete were covered in some detail in this work. This is something that needs to be pursued further however, particularly the testing aspect. In order to assure both a quality product and the safety of the workers it is essential that there be very good quality control on the concrete.

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