Period #10 Notes: ADMIXTURES & CEMENT REPLACEMENT MATERIALS

A. Brief Review

Previously, the composition of portland cement was discussed, and also the hydration reaction. One of the beautiful aspects of portland cement is that when mixed with water, it becomes a liquid fresh cement paste that takes the shape of any forms into which it is placed. Then the hydration reaction occurs, transforming the paste from a liquid into a solid.

If an excessive amount of water is added to the mix to increase its fluidity, then the hydrated cement paste (hcp) will have a high degree of capillary porosity. Since the capillary pores can be quite large, the high degree of capillary porosity, greatly weakens the hcp. This is why concrete from mixes with high water-cement ratios tends to be weaker than concrete from mixes with water-cement ratios in the vicinity of 0.40 to 0.50.

B. Admixtures

Admixtures are chemicals added to concrete mixes either during the mixing phase or at the job site to achieve desired effects. They are typically added only in small quantities (≤1-2% of the cement mass). Following is a brief description of some of the more common admixtures and the effects they yield.

1. Plasticizers: These admixtures are often called "workability aids" or "water-reducers."

- Their purpose is to increase the fluidity or workability of the fresh concrete without increasing the water-cement ratio which would weaken the concrete. These chemicals are generally vinyl based *phthalates*, which have the consistency of vegetable oil.
- Water reducing admixtures require 5-10% less water to make a concrete of equal slump, or increase the slump of concrete at the same water content. They can have the side effect of changing initial set time. Therefore, they are often added at the job site.

- Water reducers are mostly used for hot weather concrete placing and to aid pumping. A water-reducer plasticizer, however, is a hygroscopic powder, which can entrain air into the concrete mix via its effect on water's surface tension, thereby also, obtaining some of the benefits of air-entrainment (see below).

2. <u>Super plasticizers</u>: These admixtures are sometimes called high-range water reducers and are similar to plasticizers except that they greatly reduce the amount of water needed in a mix.

- High range water reducers are admixtures that allow 12-30% water reduction or greater flowability (as defined by the manufacturers, concrete suppliers and industry standards) without substantially slowing set time or increasing air entrainment.

- Each type of super plasticizer has defined ranges for the required quantities of concrete mix ingredients, along with the corresponding effects. They can maintain a specific consistency and workability at a greatly reduced amount of water. Dosages needed vary by the particular concrete mix and type of super plasticizer used. They can also produce a high strength concrete. As with most types of admixtures, super plasticizers can affect other concrete properties as well. The specific effects, however, should be found from the manufacturer.

- The effect of superplasticizers lasts only 30 to 60 minutes, depending on the brand and dosage rate, and is followed by a rapid loss in workability. As a result of the slump loss, superplasticizers are usually added to concrete at the jobsite.

3. <u>Retarding admixtures</u>: Retarding admixtures slow down the initial hydration of cement, lengthening set time. Retarders are beneficially used in hot weather conditions in order to overcome accelerating effects of higher temperatures and large masses of concrete on concrete setting time. Because most retarders also act as water reducers, they are frequently called water-reducing retarders.

- Usage of retarders helps to prevent formation of “cold joints” where the concrete sets between pours.
- As per chemical admixture classification by ASTM C 494, type B is simply a retarding admixture, while type D is both retarding and water reducing, resulting in concrete with greater compressive strength because of the lower water-cement ratio.
- Retarding admixtures consists of both organic and inorganic agents. Organic retardants include unrefined calcium, sodium, NH4, salts of lignosulfonic acids, hydrocarboxylic acids, and carbohydrates. Inorganic retardants include oxides of lead and zinc, phosphates, magnesium salts, fluorates and borates. As an example of a retardant's effects on concrete properties, lignosulfate acids and hydroxylated carboxylic acids slow the initial setting time by at least an hour and no more than three hours when used at 65-100°F.

4. <u>Accelerating admixtures</u>: Accelerators shorten the set time of concrete, allowing a cold-weather pour, early removal of forms, early surface finishing, and in some cases, early load application. Proper care must be taken while choosing the type and proportion of accelerators, as under most conditions, commonly used accelerators cause an increase in the drying shrinkage of concrete.

- Calcium chloride is a common accelerator, used to accelerate the time of set and the rate of strength gain. It should meet the requirements of ASTM D 98. Excessive amounts of calcium chloride in concrete mix may result in rapid stiffening, increase in drying shrinkage and corrosion of reinforcement. In colder climates, calcium chloride should not be used as an anti-freeze. Large amount of calcium chloride is required to lower the freezing point of the concrete, which may ruin the concrete.
- Due to the problems that calcium chlorides create with increased shrinkage and corrosion of reinforcing steel, alternatives such as triethanolamine, sodium thiocyanate, calcium formate, calcium nitrite, and calcium nitrate are preferred.

5. Air-entraining admixtures: Air-entraining agents entrain small air bubbles in the concrete. The major benefit of this is enhanced durability in freeze-thaw cycles, especially relevant in cold climates and concrete subject to exposure to moisture.

- While some strength loss typically accompanies increased air in concrete, it generally can be overcome by reducing the water-cement ratio via improved workability (due to the air-entraining agent itself) or through the use of other appropriate admixtures.
- When water freezes it expands 9% in volume. When water migrates into pcc and then freezes, its expansion puts the surrounding material into tension, creating cracks. Under repeated freezing and thawing cycles, pcc can be severely degraded prematurely. The entrained air-voids in the pcc function as small cavities into which the ice expands, eliminating tensile stresses that fracture the concrete.
- The entrained air-voids do not cluster and tend to be isolated in the concrete. For this reason, they do not significantly increase the permeability of the concrete.
- Typically 4-7% entrained air-void content in pcc is sufficient to achieve the desired effect in protecting against freeze-thaw damage.

C. Cement Replacement Materials

Cement replacement materials are special types of naturally occurring materials or industrial waste products that can be used in concrete mixes to partially replace some of the portland cement.

Cement replacement materials are frequently called *fine minerals* or *pozzolans*.

Surprisingly, concrete with cement replacement materials can actually be stronger and more durable than concrete with ordinary portland cement (opc).

The three most-commonly used cement replacement materials are the following:

1. Fly ash is a fine, glass-like powder recovered from gases created by coal-fired electric power generation. U.S. power plants produce millions of tons of fly ash annually, which is usually dumped in landfills. Fly ash is an inexpensive replacement for portland cement used in concrete, while it actually improves strength, segregation, and ease of pumping of the concrete. Fly ash is also used as an ingredient in brick, block, paving, and structural fills.

- Fly ash concrete was first used in the U.S. in 1929 for the Hoover Dam, where engineers found that it allowed for less total cement. It is now used across the country. Consisting mostly of silica, alumina and iron (Table 10.1), fly ash is a pozzolan--a substance containing aluminous and silicious material that forms cement in the presence of water. When mixed with lime and water it forms a compound similar to portland cement. The spherical shape of the particles reduces internal friction thereby increasing the concrete's fluidity, permitting longer pumping distances. Improved workability means less water is needed, resulting in less segregation of the mixture. Although fly ash cement itself is less dense than portland cement, the produced concrete is denser and results in a smoother surface with sharper detail.
- As will be discussed later, sulfates that exist in fertilized soils and coastal areas get into pcc and attack the hcp. Usage of fly ash as a cement replacement material improves resistance to sulfate attack:
  - Class F fly ash, with particles covered in a kind of melted glass, greatly reduces the risk of expansion due to sulfate attack, is produced from Eastern coal.
  - Class C fly ash produced from western coal, is also resistant to expansion from chemical attack, and has a higher percentage of calcium oxide, and is more commonly used for structural concrete.

- Because fly ash comes from various operations in different regions, its mineral makeup may not be consistent; this may cause its properties to vary, depending on the quality control of the manufacturer. There are some concerns about freeze/thaw performance and a tendency to effloresce, especially when used as a complete replacement for portland cement.
- The Clean Air Act of 1990 requires power plants to cut nitric oxide emissions. To do so, plants restrict oxygen, resulting in high-carbon fly ash, which must be reprocessed for cement production. Thus, fly ash could be less available or more costly in the future. Researchers are studying why the unprocessed high-carbon ash doesn't work for cement, and other treatment options.

2. Ground granulated blast-furnace slag (ggbs): Ground granulated blast-furnace slag is the granular material formed when molten iron blast furnace slag is quenched. It is a granular product with very limited crystal formation, is highly cementitious in nature and, when ground to cement fineness, hydrates like portland cement.

- Blast furnace slag cement, which is made by intergrinding the granulated slag with portland cement clinker (blended cement), has been used for more than 60 years. The use of separately ground slag combined with portland cement at the mixer as a mineral admixture did not start until the late 1970s.
- ASTM C 989-82 and AASHTO M 302 were developed to cover ground granulated blast furnace slag for use in concrete and mortar. The three grades are 80, 100, and 120.

- The grade of a ground granulated blast furnace slag is based on its activity index, which is the ratio (in percent) of the compressive strength of a mortar cube made with a 50 percent ggbs, 50% opc blend to that of a mortar cube made with 100% opc.
  - The use of grade 80 ground granulated blast-furnace slag should be avoided unless warranted in special circumstances since it will have a lower compressive strength at all ages. The typical justification for using grade 80 ggbs is that it has a lower heat of hydration which is important in massive concrete pours.
  - Substitution of grade 100 ground granulated blast furnace slag will generally yield an equivalent or greater strength at 28 days.
  - For a given mix, the substitution of grade 120 ground granulated blast furnace slag for up to 50 percent of the cement will generally yield a compressive strength at 7 days and beyond equivalent to or greater than that of the same concrete made without ground granulated blast furnace slag.

3. <u>Condensed Silica Fume</u> (csf). Silica fume, also known as microsilica, is a byproduct of the reduction of high-purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys. Silica fume is also collected as a byproduct in the production of other silicon alloys such as ferrochromium, ferromanganese, ferromagnesium, and calcium silicon. Before the mid-1970s, nearly all silica fume was discharged into the atmosphere. After environmental concerns necessitated the collection and landfilling of silica fume, it became economically justified to use in various applications.

- Silica fume consists of <u>very fine</u> vitreous particles approximately 100 times smaller than those of ordinary cement particles, and with a surface area on the order of 20,000 m^2/kg (Table 10.2). Because of its extreme fineness and high silica content, csf is a highly effective pozzolanic material.

- It has been found that csf: improves compressive strength, bond strength, and abrasion resistance; reduces permeability; and therefore helps in protecting reinforcing steel from corrosion.
- Csf has been used at cement replacement rates of up to 15%, although the normal rate is 7-10% percent. With 15% replacement, the potential exists for very strong, brittle concrete.
- Due to its extreme fineness, csf reduces the fluidity (slump) of fresh concrete. It therefore increases the water demand in a concrete mix such that for each 1 kg of csf used, the mass of water must be increased by 1 kg.
- Usage of cfs at rates of less than 5% will not typically require a water reducer. Higher replacement rates will require the use of a high range water reducer.

Table 10.1 Percent composition of cement replacement materials by mass. (Illston, 1994)

Oxide	pfa		ggbs	csf	Portland cement (Type I)
	Low lime	High lime			
SiO_2	48	40	36	97	20
Al_2O_3	27	18	9	2	5
Fe_2O_3	9	8	1	0.1	4
MgO	2	4	11	0.1	1
CaO	3	20	40		64
Na_2O	1	--	--		0.2
K_2O	4	--	--		0.5

Table 10.2. Typical physical properties of cement replacement materials (Illston, 1994).

	pfa	ggbs	csf	opc
Specific gravity	2.1	2.9	2.2	3.15
Particle size range (μm)	10-150	3-100	0.01-0.5	0.5-100
Specific surface area (m^2/kg)	350	400	15,000	350