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Admixtures and Ground Slag for Concrete

**COMMITTEE ON
CHEMICAL ADDITIONS AND ADMIXTURES FOR CONCRETE
H. Celik Ozyildirim, Chairman**

William F. Boles
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Raymond J. Schutz
Maris A. Sermolins

A. Haleem Tahir
Suneel N. Vanikar
David Whiting

Transportation Research Board Staff: Frederick D. Hejl

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ADMIXTURES AND GROUND SLAG FOR CONCRETE

TRANSPORTATION RESEARCH BOARD/NATIONAL RESEARCH COUNCIL

PREFACE

This report was prepared by the Transportation Research Board Committee on Chemical Additions and Admixtures for Concrete (A2E05). It is intended to provide practical information on admixtures and slag to practitioners dealing with concretes in the transportation field.

The report supersedes information in Special Report 119 published in 1971 on accelerating, air-entraining, water-reducing, and pozzolanic (Type F fly ash) admixtures. In addition, it includes information concerning latex, high-range water-reducing, corrosion-inhibiting, Type C fly ash, and silica fume pozzolanic admixtures and slag. The summary table in Chapter 1 provides a quick reference concerning major expected advantages and possible detrimental effects but should not be construed as being all inclusive.

Significant contributions were made by past and present members of the Committee and other knowledgeable persons in the field. The Committee hopes to continue updating this document as new information is developed. Comments from users will be greatly appreciated.

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CHAPTER 1: INTRODUCTION

General Description

There is a growing use of various types of admixtures and ground granulated iron blast-furnace slag in hydraulic cement concrete. When properly used, such materials can enhance desirable characteristics of both unhardened and hardened concrete.

An admixture is defined by the American Concrete Institute (ACI 116R) as: "a material other than water, aggregates, hydraulic cement and fiber reinforcement used as an ingredient of concrete or mortar, and added to the batch immediately before or during its mixing." Because of its hydraulic cementing properties, ground granulated iron blast-furnace slag, referred to as slag herein, is not an admixture by this definition, but is included in this report because of its frequent use as a cementitious material added to the batch at the concrete mixing plant. Some Class C fly ashes also have cementitious properties, but these generally are referred to as pozzolanic admixtures.

Admixtures are of various types and are used for a number of purposes (1,2,3). They may be chemicals added in small amounts, usually as a liquid, or products added in relatively larger quantities as a pozzolanic or cementitious ingredient of the concrete. Some materials contribute substantially to the strength development of the concrete, but others, such as coloring agents, may be chemically inert. Some chemical admixtures impart beneficial properties to the concrete during placement and early stages of hydration but have the potential to adversely affect strength and other properties of the hardened concrete. In other cases an admixture may perform in a predictable manner for a given set of circumstances but can cause problems under a different set of circumstances. Such changes in performance result from complex chemical reactions between the admixture and the concrete ingredients, and the effect of ambient conditions during or after placement.

Concrete technologists recommend that for a specific project, the performance of the admixture(s) should be observed in trial mixtures using the intended concrete ingredients, including all admixtures, and in environmental conditions simulating those expected during construction. In trial mixtures, the optimum amounts of the chemical admixtures (dosage) should be determined by observing the effects of varied dosages on the concrete properties. Dosage rates should be adjusted on the basis of field experience for the conditions existing during construction, especially

when field conditions are different from the laboratory conditions under which the dosage rate was established. It is also essential that when changes in admixture dosage are made, properties of the hardened concrete be closely monitored.

When material such as slag, silica fume, and fly ash are used, the optimum proportions to obtain the desired characteristics of the hardened concrete should be determined by the trial mixtures. Chemical admixtures needed to adjust the characteristics of concretes containing these cementitious materials may also be subject to change depending on field conditions.

In the following chapters, the major classes of admixtures and slag materials that are used or have a potential for use in the construction of highways and bridges are discussed. In a number of cases these materials are expensive and are applicable only for special situations. Costs will vary greatly depending on availability in different locations, and economic evaluations must be made on a case-by-case basis.

The information presented includes the reasons for their use, the expected effects on concrete, and precautions concerning unwanted side effects of these materials. To the extent possible, specific references to the sources of information are cited and listed at the end of each chapter. Many of the general statements about behavior or use represent a consensus of a number of published sources and the experience of persons actively engaged in concrete technology.

Summary of Advantages and Disadvantages

Table 1.1 is a general summary of the expected beneficial effects and potential detrimental effects of admixtures and slag.

References

1. Ramachandran, V.S. ed., *Concrete Admixtures Handbook*, Noyes Publications, 1984.
2. Rixom, M. R., and Mailvaganam, N. P., *Chemical Admixtures for Concrete*, Second Edition, E. & F. N. Spon, New York, 1986.
3. ACI 212, Guide for Use of Admixtures in Concrete, *ACI Manual of Concrete Practice, Part 1*.

TABLE 1.1: Beneficial and Detrimental Effects of Admixture and Slag on the Properties of Concrete

Class or Type of Material	Beneficial Effects	Detrimental Effects
Air- Entraining	<ol style="list-style-type: none"> 1. Improves resistance to freezing and thawing. 2. Improves resistance to deicers. 3. Improves workability. 4. Reduces segregation and bleeding, particularly in concretes with low cement contents. 5. Reduces mixing water requirement significantly in concretes with low cement content. Little reduction is expected in concretes with high cement content (>700 lb/cy). 6. Reduces permeability by reducing w/c. 	<ol style="list-style-type: none"> 1. May reduce strength unless w/c is appropriately lowered. At constant slump strength may increase for concretes with low cement factor (<400 lb/cy) and decrease approximately 5 percent for each 1 percent air for concretes with higher cement factors.
Water- Reducing (normal and high range)	<ol style="list-style-type: none"> 1. Improves compressive strength because of reduced w/c. 2. Improves workability with constant water content. May increase rate of hydration during initial hydration. 3. Achieves workability and required strength at lower cement contents. 4. Reduces permeability when w/c is reduced. 5. Improves consolidation at constant water content. 	<ol style="list-style-type: none"> 1. At constant slump hydroxylated types generally increase bleeding (ligno-sulfonate types reduce bleeding). 2. Concretes with low and moderate slumps may be difficult to finish because of stickiness. 3. Can accelerate rate of slump loss causing rapid loss of workability. 4. Can retard setting especially at high dosages. 5. May increase size of air voids especially when HRWR is used. 6. May slightly increase creep or shrinkage.

TABLE 1.1: Beneficial and Detrimental Effects of Admixture and Slag on the Properties of Concrete (Continued)

Retarding	<ol style="list-style-type: none"> 1. Delays setting. 2. Minimizes potential for cold joints. 3. Extends time for concrete placement and finishing. 	<ol style="list-style-type: none"> 1. Excessive dosage rate may excessively delay hardening. 2. Increases bleeding. 3. Effectiveness reduced when used with cements having high alkali and C_3A contents.
Accelerating	<ol style="list-style-type: none"> 1. Reduces time of setting. 2. Increases initial rate of strength development. 	<ol style="list-style-type: none"> 1. Excessive dosage rate may reduce setting time excessively or produce flash set. 2. Increases drying shrinkage and creep. 3. May reduce ultimate strength. 4. May aggravate corrosion of reinforcement. 5. Calcium chloride increases tendency for alkali aggregate reaction. 6. Calcium chloride decreases sulfate resistance of non-sulfate-resisting cement concretes.
Fly Ash	<ol style="list-style-type: none"> 1. Increases workability at constant water content depending upon fineness and increase in total cement plus fly ash content. 2. Reduces bleeding and segregation. 3. Improves pumpability. 4. Can reduce heat evolution during hardening, particularly with low CaO fly ash. 5. Increases strength gain at later ages, depending on the CaO content. 6. Decreases permeability after proper curing. 7. May improve durability. 	<ol style="list-style-type: none"> 1. Increases times of setting, particularly in cold weather. 2. Increases amount of air-entraining admixture required for constant air content, as a function of carbon content. 3. Loss of air content may occur during continued mixing and elongation. 4. Slower early strength gain. 5. May require longer curing periods.

TABLE 1.1: Beneficial and Detrimental Effects of Admixture and Slag on the Properties of Concrete (Continued)

	8. Can aid in reducing effect of alkali-aggregate reactions.	6. May be more susceptible to surface scaling from deicing salts.
Silica Fume	<ol style="list-style-type: none"> 1. Increases strength. 2. Increases electrical resistivity. 3. Reduces bleeding and segregation. 4. Decreases permeability. 5. Improves sulfate resistance. 6. Reduces alkali-aggregate reactivity. 7. Improves abrasion resistance. 8. Generally improves resistance to many chemical solutions, including deicing salts. 9. Increases bond strength. 	<ol style="list-style-type: none"> 1. More susceptible to plastic shrinkage cracking. 2. High water demand. Needs water-reducing admixture (usually HRWR) to compensate for the increase. 3. Exhibits a darker color. 4. Can be difficult to finish because of fineness and lack of bleeding.
Slag	<ol style="list-style-type: none"> 1. Increases workability. 2. Delays time of setting. 3. Reduces bleeding and segregation. 4. Increases strength beyond 7 days. 5. Exhibits lighter color. 6. May improve resistance to sulfates. 7. Improves resistance to alkali-aggregate reactivity. 8. Reduces heat rise. 9. Reduces permeability. 10. Achieves rapid strength gain with accelerated curing. 	<ol style="list-style-type: none"> 1. Sets slower, especially in cold weather. 2. May require more air-entraining admixture. 3. Reduces strength gain at early ages. 4. Exhibits a color difference. Temporary blue-green-tint at early ages. 5. May have greater shrinkage.
Latex	<ol style="list-style-type: none"> 1. Improves workability. 2. Reduces tendency of microcracks to propagate and provides high failure strain. 3. Improves durability by restricting penetration of aggressive agents. 4. Improves adhesion of thin sections. 5. Reduces permeability. 	<ol style="list-style-type: none"> 1. May need antifoaming agent to suppress air entrainment. 2. Hydrolysis of certain polymers in moist concrete and alkaline environment may produce loss in strength. 3. Often lowers modulus of elasticity.

TABLE 1.1: Beneficial and Detrimental Effects of Admixture and Slag on the Properties of Concrete (Continued)

		<ol style="list-style-type: none"> 4. Increases drag on finishing tools. 5. Requires more careful attention to finishing. 6. Cannot be used below minimum film forming temperature. 7. Not suitable for underwater applications.
Corrosion Inhibitors	<ol style="list-style-type: none"> 1. Delays corrosion of reinforcing steel. 2. Inhibits corrosion depending upon ration of corrosive ions to inhibitor. 3. May accelerate time of setting. 	<ol style="list-style-type: none"> 1. Accelerated setting may need to be controlled by retarders. 2. May require higher amounts of air-entraining admixture to obtain the air-void system required for adequate resistance to freezing and thawing.

CHAPTER 2: AIR-ENTRAINING ADMIXTURES

General

The purpose of intentionally entraining air in concrete is to increase its resistance to damage from freezing and thawing and thus improve its durability. The purpose of the air-entraining admixture (AE) is to stabilize the desirable air bubbles formed during the mixing of the concrete. It is important that the amount of air, the size of air bubbles, and their stability be properly controlled to achieve optimum concrete properties.

Description

Composition

Most AEs are organic materials generally classified as surface-active agents or surfactants. Surfactants are generally characterized by a structure which is essentially linear and in which each end of the molecule has a distinct character. One end is normally hydrophilic (i.e., has an affinity for water). The other end is generally hydrophobic (repels water). The hydrophilic end can be anionic (negatively charged), cationic (positive charged), or nonionic (neutral). The most frequently encountered groups are anionic which may be either carboxylic (COOH) or sulfonic (SO₃H) types.

Types

AEs are derived from a number of sources (1). The most widely used, and the oldest air-entraining formulations, are based on neutralized vinsol resin. Vinsol resin is a by-product of a process for recovering various solvents and rosins from pine wood stumps (2).

Vinsol resin is available in pulverized and flake forms. It is essentially insoluble in water. In order to function effectively as a concrete admixture, vinsol resin is converted into a soluble form by neutralizing with sodium hydroxide so as to form a water-soluble soap. End users generally purchase formulated vinsol resin products which may contain from 8 to 15 percent active ingredients.

A second major category of AEs are the petroleum-derived products. These fall into the general chemical group of aryl-alkyl-sulfonate and

are marketed as synthetic AEs. However, the user should be aware that a "synthetic" or "aryl-alkyl-sulfonate" AE from one manufacture may be completely different from one marketed by another manufacturer under the same broad generic description.

The fatty and resinous acids and their salts are derived from the processing of animal and vegetable fats and oils either by direct saponification of the crude materials, or sulfonation followed by distillation under vacuum to separate the individual acids (3). These fatty acids are characterized by a long hydrocarbon chain which terminates in a carboxylic (COOH) end group. The most important acids are those saturated acids ranging from the C₁₂ through C₁₈ position.

Specifications

The standard specification for AE for concrete is ASTM C 260. This is basically a performance specification and does not restrict the types of material used. However, a manufacturer must certify that material furnished for a job is the same as the material for which test results are available. The test methods used to test AE for concrete are included in ASTM Method C 233 (AASHTO T 157).

Mechanism of Action

Entrained air is produced by the mechanical stirring, kneading, and infolding actions of a concrete mixer. The exact nature of the action is a function of the particular type and geometry of the mixer being used. Powers (4) has suggested that mixers of the drum type (such as used in the ready-mix industry) owe much of their ability to entrain air to the stirring or kneading action as the batch falls between the baffles in the drum and entrapped air is broken up and dispersed into the system as air bubbles. The AE acts to stabilize these bubbles after they have been formed.

The AE functions in two ways. It reduces the surface tension of water, thus enabling the shear stresses developed by the mixer to create small bubbles, and it stabilizes the bubbles. It is postulated that the ionizable ends of AEs are

attracted to the cement surface, and their hydrophobic ends protrude into the air bubbles (5,6). Cement grains are usually smaller than the air bubbles, thus the cement tends to form a layer of particles around each bubble. This layer is relatively thick and cohesive, and it imparts a high degree of stability to the otherwise fragile air-water interface.

Stability of Entrained Air

One problem generally encountered in freshly mixed concrete is the gradual loss of air content with time. Air contained within the bubbles is subjected to significant interfacial pressure because of surface tension. This pressure increases solubility, and it is the smaller bubbles that are most affected. It is imperative that these bubbles be stabilized to avoid the tendency to dissolve into the mixing water with subsequent loss of entrained air.

Research has shown that some AEs are more effective than others in stabilizing the smaller voids (7,8). The effectiveness is related to a number of complex parameters, but the role of each parameter has not been fully explained.

Air-Void System in Hardened Concrete

Air bubbles formed in freshly mixed concrete persist throughout the setting of the concrete and remain as a fine structure of spherical voids in the final, hardened state. This structure is commonly termed the "air-void system" of hardened concrete. The majority of these voids generally fall into the size range 10 to 1,000 or 2,000 micrometers with the peak in the void size distribution commonly found at diameters less than 100 micrometers.

The techniques most commonly used for determination of air content in hardened concrete and other void system parameters are the linear traverse and the point-count methods described in ASTM C 457 "Standard Recommended Practice for Microscopical Determination of Air-Void Content and Parameters of the Air-Void System in Hardened Concrete." This practice describes the procedures for determining several parameters for judging the adequacy of the air-void system in hardened concrete. These are: (a) the total air content; (b) the specific surface of the air voids; and (c) the spacing factor.

Requirement for Optimum Protection

As previously stated, the primary purpose for incorporating entrained air in concrete is for protection against deterioration due to freezing and thawing. The process of freezing within the capillary system of concrete leads to generation of expansive forces that are sufficient to cause failure of the cement paste. Although complex theories have been developed to explain and predict the effectiveness of air entrainment, the generally accepted simplified mechanism is that the air voids provide spaces into which water may be forced (or ice may grow) during freezing and thawing, thus preventing the build-up of high pressures (9,10,11). The air contained in the voids is compressible and can accommodate volumetric changes during expansion.

Studies relating to the determination of the air content and the optimum spacing of the air voids have demonstrated that there is an optimum amount of air (assuming an acceptable void size distribution) above which further increase does not materially increase the durability of the concrete (12,13). The optimum amount varies with maximum size of aggregate in the concrete mixture. However, when expressed as a function of the mortar content, the optimum air content is generally in the range of 9 plus or minus 1 percent of the mortar volume. Another important finding is that concretes not given an air drying period prior to test are not as resistant to freezing and thawing in water as those that are air dried. Other work has shown that durability decreases greatly as the water-cement ratio (w/c) is increased from 0.35 to 0.85 (14).

The American Concrete Institute (ACI) has developed guidelines for levels of air content needed to protect concrete under various severities of freeze-thaw environments. Table 2.1, reproduced from ACI 201.2R, summarizes the recommended levels for different conditions and aggregate sizes (15).

In addition to the optimum percentage of entrained air, the spacing factor, specific surface, and number of voids per unit volume are important. These parameters often are better indicators of durability than the overall air content of the concrete (7,12). Current ACI recommendations for bridge deck construction (16) pertaining to air-void

TABLE 2.1 Recommended Air Contents for Frost-Resistant Concrete

<u>Nominal Maximum Aggregate</u>		<u>Average air content, percent*</u>	
<u>size, in.</u>	<u>(mm)</u>	<u>Severe exposure**</u>	<u>Moderate exposure***</u>
3/8	(9.5)	7 1/2	6
1/2	(12.5)	7	5 1/2
3/4	(19)	6	5
1 1/2	(38)	5 1/2	4 1/2
3****	(75)	4 1/2	3 1/2
6****	(150)	4	3

*A reasonable tolerance for air content in field construction is plus or minus 1 1/2 percent.

**Outdoor exposure in a cold climate where the concrete may be in almost continuous contact with moisture prior to freezing, or where deicing salts are used. Examples are pavements, bridge decks, sidewalks, and water tanks.

***Outdoor exposure in a cold climate where the concrete will be only occasionally exposed to moisture prior to freezing and where no deicing salts will be used. Examples are certain exterior walls, beams, girders, and slabs not in direct contact with soil.

****These air contents apply to the whole mix, as for the preceding aggregate sizes. When testing these concretes, however, aggregate larger than 1 1/2 in. (38 mm) is removed by handpicking or sieving and the air content is determined on the minus 1 1/2 in. (38 mm) fraction of the mix. (The field tolerance applies to this value.) From this the air content of the whole mix is computed.

There is conflicting opinion on whether air contents lower than those given in the table should be permitted for high strength (more about 5500 psi) (37.8 MPa) concrete. This committee believes that where supporting experience and/or experimental data exists for particular combinations of materials, construction practices, and exposure, the air contents may be reduced by approximately 1 percent. {For maximum aggregate sizes over 1 1/2 in. (38 mm), this reduction applies to the minus 1 1/2 in. (38 mm) fraction of the mix.}

NOTE: The above table was reproduced from ACI 201.2R.

characteristics call for a spacing factor less than 0.008 in. (0.2 mm) and a specific surface greater than 600 in $^2/\text{in}^3$.

Effects of Ingredients on Dosage Rates

Cement Content

As the cement content of a concrete mixture is increased, not only does the net amount of the AE per cubic yard increase as would logically be expected, but the proportional amount of AE per unit weight of cement also increases (17). Therefore, it is necessary to determine air contents when changes are made in the types and proportions of ingredients.

Cement Composition

The predominant factor related to the influence of chemical composition of cement on air entrainment is the alkali content of the cement. This can range from low values of near 0.1 percent to somewhat greater than 1 percent. Generally, it has been shown that an increase in cement alkali content will increase air content in concrete for a given dosage of AE when other factors are constant (18).

Aggregate Proportions and Grading

An increase in the maximum size of coarse aggregate results in a decreased mortar content. Since entrained air is contained wholly within the mortar fraction, a given dosage of AE results in an increase in air content of the mortar when the size of the aggregate is increased. Also the requirement for the amount of air per volume percentage of concrete decreases as the aggregate size increases because of a lower amount of mortar in the concrete.

Fine aggregate itself contributes to air entrainment by retention of air bubbles within the interstitial voids between the fine aggregate particles. Fine aggregates which increase the air content of mixtures not containing an AE will likewise yield mixtures having high air contents when the AE is added to the batch (19). An increase in air content of about 1 percentage point for every 10 percent increase in fine aggregate content is typical. For a given total fine aggregate content an increased

amount of fines passing No. 200 sieve will increase the required dosage of AE. Alternately, an increased amount of No. 30 to No. 50 sizes will decrease the dosage.

Slump

The slump of concrete has a significant effect on air content. In most cases the air content will increase with an increase in the slump. The sensitivity of this effect is apparently a function of the particular AE being used. Above a slump of 6 to 7 inches many mixtures become too fluid to retain entrained air. In the range of about 1/2 to about 5 inches each 1 inch increase in slump is accompanied by an increase of about 1/2 percentage point in air content. Further increases in slump are accompanied by a rapid decrease in air content. At very low slumps (less than 1 inch), satisfactory air content and air-void system can be obtained but is difficult. Dosages of AE may range up to 10 times those normally needed (21). In very stiff mixtures it is possible to entrain air with less change in the dosage of AE by mixing in two stages: entraining air in the mortar fraction, and then adding the coarse aggregate. Mixer design and intensity may become a critical factor in such mixtures.

Water-Reducing and Retarding Admixtures

It is generally recognized that for most water reducing and retarding admixtures, less AE is needed to achieve a given specified air content. This is true even for those materials that do not in themselves contribute toward increase in air content when no AE is used. In one study (21) it was found that the amount of AE needed to obtain air contents of 5 to 6 percent ranged from zero to about 85 percent of the control amount, depending on the admixture used (21). Most lignosulfonates required from about 10 to 50 percent of the control amount of AE to achieve the desired air content. The organic-acids on the average required higher percentages of AE ranging from about 160 to 180 percent of control.

Not only is the gross air content influenced by the introduction of water-reducing and retarding admixtures into air-entrained concrete, but the parameters of the air-void system are affected as well. A study of three water-reducing, set-retarding admixtures on the parameters of the air-void system

using three dosages of admixtures corresponding to normal dose, double dose, and quadruple dose of admixture has shown that the amount of AE needed to achieve a desired air content of 5 to 7 percent generally decreases with increasing dosage for each of the water-reducing admixtures (22). Spacing factors increased with an increase in dosage. Specific surfaces generally decreased with an increase in dosage because of larger air bubbles.

Accelerating Admixtures

Most of the information available regarding effects of the accelerators on air entrainment relates to the use of calcium chloride. For a fixed amount of AE, the effect of adding the normally used amount of calcium chloride is to slightly increase the air content, by at most one percentage point. When air is being held to a specific level, the dosage of AE needed to achieve this level is decreased as calcium chloride is added. It has been suggested that the dosage of AE be reduced by 40 percent for low alkali and 5 to 10 percent for high alkali cements when calcium chloride is used (17).

High-Range Water-Reducing Admixtures

Because the high-range water-reducing admixture (HRWR) has a significant effect on concrete slump, the factors already mentioned may significantly affect the amount of AE (23,24). Therefore, trial mixtures are necessary to determine the proper dosage of AE when HRWR is used.

Pozzolans

The finely divided mineral admixtures and cementitious materials used in concrete may affect air-void characteristics. These include fly ash, slag, silica fume, volcanic glass, diatomaceous earth, calcined shales, clays, and others.

It is generally accepted that the majority of very fine materials will increase the amount of AE needed to obtain a specified percentage of air in the concrete when compared to a similar concrete mixture not containing such materials. The effects of fly ash, silica fume, and slag on the amounts of AE needed for concretes containing these materials are discussed in Chapters 7 and 8.

Effects of Placement Procedures on Air Content

Production Procedures

In the batching process, the sequence of AE addition affects the amount of air. Simultaneous batching will lower the air content, and the late addition of AE raises the air content. In the mixing process, there is an optimum time of mixing and mixing speed for the achievement of proper air content. Also, long hauls will reduce air content, especially in hot weather (25).

Construction Practices

Retempering increases the air content. Pumping and prolonged vibration decreases it. Excessive finishing reduces the air content at the surface layer. The temperature of the environment also affects the air content: an increase in temperature causes a reduction in air content (25).

Effects of Entrained Air on Unhardened Concrete

Entrained air bubbles act as a lubricant in freshly mixed concrete. In harsh concretes with low cement content, inclusion of entrained air significantly reduces the amount of mixing water required to produce a given slump. This is similar to the effect of adding more cement, fly ash or 75 μm (No. 200) fines. All lubricate the mixture and decrease the required mixing water content.

However, in mixtures with 600 or more pounds of cement per cubic yard, the mixture has adequate cohesiveness and the addition of further fines tends to increase the mixing water requirement. In such mixtures, the addition of air is much less effective in increasing the slump or reducing the mixing water requirement. Naturally, throughout the usual range of air contents, the initial percentages of air are more effective in reducing mixing water than subsequent additional amounts.

These effects of air on mixing water required for constant slump are such that in lean mixtures the incorporation of modest amounts of air can overcome the potential strength loss of 5 percent for each percent of air added and produce an actual increase in strength by reducing the w/c (26). In the high cement content mixtures, the reduction in mixing water is negligible, and the strength loss due

to incorporation of air is significant. Also, in these rich mixtures, increasing the cement fines increases the required water content such that the additional cement may fail to reduce the w/c. In this circumstance, strength will reach a maximum, and chemical or mineral admixtures must be used to further increase the strength or reduce the w/c.

Naturally, these effects of air on the required mixing water depend to some extent on the particle shape, surface texture, and grading of the fine aggregate used. Very angular fine aggregates benefit more from the use of air entrainment, and the benefits extend to higher levels of cement and air content.

In proportioning concrete mixtures for inclusion of entrained air, the volume of air added replaces some portions of the mixing water, which must be reduced to maintain slump, and the remaining volume is removed from the fine aggregate. That is, air replaces fine aggregate and water on an absolute volume basis.

Entrained air will reduce bleeding and often encourages early finishing (27). It will aggravate blistering and delamination in steel-trowelled concrete and concrete where a dry shake is applied.

Effects of Entrained Air on Hardened Concrete

Resistance to Freezing and Thawing

Concrete is air-entrained primarily to increase its resistance to freezing and thawing, and deicer scaling. Entrained air will not protect concrete made with coarse aggregate that is not resistant to freezing and thawing, but it does protect the mortar phase containing acceptable fine aggregates. The mechanism involved and the optimum values of the critical parameters have been discussed in previous sections.

Strength

In general, an increase in air content manifests itself as a decrease in strength, presumably due to the obvious loss in solid cross-sectional area as well as the ability of air voids to function as stress concentrators in the mortar matrix. The relationship between air content and strength is influenced by the w/c. At low w/c the loss of strength is more pronounced for each increment of air content than for higher w/c (26,28).

The effect of air entrainment on strength has been shown to depend on the mixture proportions used (28). At lower cement contents air entrainment may be beneficial to strength because of reduced w/c. However, in concretes frequently used in highway work which contain between 500 and 650 lb/yd³ of cement, the following two rules of thumb have proven useful: (a) a 5 percent loss in compressive strength occurs for each additional percentage point of entrained air; and (b) for each percentage point of increased entrained air, compressive strength is reduced by 200 psi. These rules assume that there is no adjustment made to the mixture proportions in order to compensate for the increase in air content. If cement contents are low, increases in air content may allow for corresponding decrease in water content, thereby offsetting strength loss. Other studies have also shown that the loss of flexural strength has the same general tendencies with increasing cement and air content as does compressive strength, but the magnitude of the decrease is somewhat less (28).

Elastic Modulus

As with strength, an increase in the level of entrained air results in a decrease in the modulus of elasticity. Studies on concrete with various types of aggregate (29,30) over a range of air contents from 1 to 8 percent indicate an average value of 100,000 to 200,000 psi loss in static modulus for every additional percentage point of air which is entrained.

Shrinkage and Creep

Available data (31) indicate that entrained air has little affect on drying shrinkage of properly proportioned concretes. A comparison of the creep of air-entrained vs non-air-entrained concrete (32) at various strength levels showed little consistent effect of air content on creep.

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CHAPTER 3: WATER-REDUCING AND RETARDING ADMIXTURES

General

Water-reducing and retarding admixtures are used in concrete (air-entrained or non-air-entrained) either to reduce the water requirements or to retard the time of setting, or both. The use of these admixtures may result in a reduced w/c for a given workability or improved workability for a given w/c and constant cement contents. The various materials are classified on the basis of the end result desired.

Classification and Specifications

Water reducing and retarding admixtures are classified by ASTM C 494 "Standard Specification for Chemical Admixtures for Concrete" as follows:

- Type A - water-reducing
- Type B - retarding
- Type D - water-reducing and retarding
- Type F - high-range water-reducing
- Type G - high-range water-reducing and retarding

Type F and G are also covered by ASTM C 1017, which is the specification for chemical admixtures for use in producing flowing concrete. This standard includes two types - plasticizing (type 1), and plasticizing and retarding (type 2). Accelerating admixtures (Type C), and water reducing and accelerating admixtures (Type E) are covered in Chapter 4.

Composition

Various materials are used to formulate the different types of admixtures, and different combinations will be found in different commercial formulations. In general, the normal-range water-reducing admixtures will be one of several types. Those containing mostly salts and modifications of hydroxylated carboxylic acids are commonly referred to as the HC type; those containing salts and modifications of lignosulfonic acids are commonly referred to as lignins; and those containing carbohydrates and polysaccharides are commonly called polymers or PS types. HRWRs are

of different composition. These will contain salts of high molecular weight naphthalene sulfonic acid formaldehyde condensates, and salts of melaminesulfonic acid formaldehyde condensates, or salts and modifications of ligninsulfonic acids.

Both the normal-range water-reducing admixtures and the HRWRs function by dispersing the cement particles and making the paste in concrete fluid. The significant difference between the two is that HRWR can be added at high dosage rates without having an unacceptable effect on the time of setting or air content. Two chemical families are commonly used for this purpose in HRWR. The formaldehyde condensates of naphthalene or melamine sulfonic acid are the basis for the high-range water reducers "superplasticizers" (ASTM C 494, Types F and G). These molecules contain no hydroxyl groups and therefore, these admixtures can be used at very high dosage rates to obtain very high water reductions and can be redosed without excessive retardation.

The salts of lignosulfonic acid contain both hydroxyl groups and sulfonic acid groups, and therefore, obtain their water-reducing properties by a combination of both mechanisms. At high dosages, these admixtures will produce the high water reductions or the high workability of the high-range water reducers. However, as one increases the dosage, the number of hydroxyl groups are necessarily increased, and extreme retardation may result.

Effects of Normal-Range Water-Reducing Admixtures on Concrete

Water Reduction

When used at the manufacturer's recommended normal dosage, the HC and PS types of admixtures reduce water demand by 5 to 8 percent. The lignin types reduce water by 7 to 10 percent. All types exhibit higher water reductions at higher dosages, however, excess retardation may be encountered. Thus for normal usage, it is important to follow the manufacturer's recommendations.

Time of Setting

A common side effect of water-reducing admixtures is a tendency to also retard the time of setting of the concrete. This effect is counteracted in Type A and Type E by adding other chemicals such as calcium chloride and ortriethanolamine to offset retardation. At normal dosages all Type D admixtures usually retard initial and final time of setting by one to three and a half hours at usual ambient temperature.

Strength

The HC, PS, and to some degree lignin types increase the strength of concrete above that resulting from the reduction in w/c (4).

Air Entrainment

The HC and PS admixtures do not entrain air per se, but since they render the concrete more workable, less AE is generally required to obtain a given air content. The normal dosage of lignin admixtures may add one to two percent of entrained air to the concrete.

Bleeding

Generally, the lignin types reduced the bleeding of the concrete, and the HC types increase bleeding.

Economy

The use of water-reducing admixtures increases strength at a given workability and cement content, thus a given strength can be obtained at a lower cement content. Because the cement saved generally costs more than the cost of the admixture, concrete of a given strength can be produced more economically. When admixtures are so used, reducing the cement content will also reduce the unit heat of hydration, which can be very desirable when placing mass concrete.

Slump Loss

All water-reduced concrete loses slump at a faster rate than equivalent concrete without the admixture. However, this does not generally create problems with the HC, PS, and lignin types.

Effects of High-Range Water-Reducing Admixtures on Concrete

General

These admixtures are powerful dispersing agents, and their action in portland cement pastes, mortars and concretes can be attributed to this action. Commercially marketed HRWR may be formulated by combining the dispersing agents with lignin, HC, or PS admixtures. These formulations may impart retardation or slightly longer setting time to the cementitious mixture.

Water Reduction

At low dosages, 0.05-0.1 percent by weight of the cement, approximately 0.6 to 1.2 oz/100 lb cement, the HRWR reduces water demand to the same extent as the conventional admixtures. However, since these admixtures are not inherently retarders, they may be used at much higher dosages. Water reductions of 20 to 30 percent are not uncommon. When used without water reduction, concrete with very high workability, often termed flowing concrete, can be produced with a relatively low w/c.

Time of Setting

When used as water reducers, the unblended naphthalene formaldehyde and melamine formaldehyde high-range water reducers will have little affect on time of setting as measured by ASTM C 403. When blended HRWR (Type G) is used with conventional admixtures, concrete may exhibit retardation of one to three and a half hours at normal ambient temperatures.

When HRWR is used to produce flowing concrete, retardation generally occurs.

Strength

Since HRWR may be used to manufacture workable concrete at very low w/c, very high strength concrete can be manufactured in the field. Compressive strengths greater than 14,000 psi at 28 days have been attained. Such low w/c concrete also will have very high-early strengths. Such high-early strength concrete is used for rapid repairs or quick reuse of forms. As an example, 3,000-psi strength can be routinely attained within 8 hours using a

HRWR to produce workable concrete at a w/c of 0.25 or lower provided that favorable temperatures are maintained.

Air Entrainment

Air-entrained concrete with HRWR generally exhibits acceptable resistance to freezing and thawing, although a coarser than normal air-void system may exist (5,6,7).

Bleeding

When HRWR is used at moderate dosages in concrete with sufficient fines (cement, fly ash, silica fume, fine aggregate) bleeding is not significantly affected. However, when used in lean concretes or concretes deficient in fines, or when used to produce flowing concrete, severe bleeding and segregation can occur. The remedy for such an occurrence is to increase the fines in the concrete by increasing the fine-to-total aggregate ratio or the cement or pozzolan content, or by decreasing the HRWR dosage.

Economy

Because of their high cost, HRWR can rarely be used to economically reduce the cement content. However, in some applications, savings in labor required to place the concrete, early stripping and the reuse of forms, or earlier use of the structure can result in overall cost reduction. Also, the use of HRWR can result in low w/c concretes which have low permeabilities. Thus, cost-effective durable concretes can be achieved.

Slump Loss

The rate of slump loss of concretes containing HRWR is greater than concrete without admixtures or concrete containing conventional admixtures (Type A). This phenomenon occurs even with the blended HRWR or so called "second" and "third generation" admixtures (8). The short working life of concrete with HRWR should be taken into consideration during the planning stage for any project; often it is best to add the HRWR admixture at the job site immediately before placement.

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CHAPTER 4: ACCELERATING ADMIXTURES

General

An accelerating admixture is a substance in liquid or solid form which, when added to concrete, either shortens the time of setting or increases the rate of hardening and strength development, or both.

Chemical Types and Mechanisms of Action

The most common accelerating admixtures are water-soluble inorganic salts; however, water-soluble organic salts are also used.

Inorganic Accelerating Admixtures

The most common inorganic accelerator is calcium chloride. It shortens the time of setting in portland cement concrete by accelerating the hydration of tricalcium and dicalcium silicate. The most common solid form of calcium chloride is flake, which is in the dihydrate form ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$). The commercial product will have an assay of 77 percent to 80 percent $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. A 29 percent solution of CaCl_2 is the most frequent form of liquid product commercially available. In solid or liquid form, the product should meet the requirements for ASTM C 494, Type C and also ASTM D 98.

It has been shown that in portland cement concrete, some of the calcium chloride combines with the tricalcium aluminate phase to form calcium chloroaluminate hydrate (1,2).

Calcium chloride may or may not be compatible with shrinkage-compensating or self-stressing cements with regard to the effect on expansion even though acceleration of setting occurs. The concrete proposed for use should be evaluated with the accelerator to determine its effect (3).

Calcium chloride should not be used with calcium-aluminate cement since it retards the hydration. It also retards setting of rapid hardening cements based on calcium fluoroaluminate.

The effects of calcium chloride on blended cements made with slags or pozzolans are similar to those on portland cements, the effects being greater for cements using ground-granulated blast-furnace slag than for those with pozzolans (4).

Calcium chloride is not recommended for use in prestressed or post-tensioned concrete, in concrete containing embedded dissimilar metals, or in reinforced concrete in a moist environment, because of its tendency to promote corrosion of steel.

Other inorganic accelerators besides calcium chloride include bromides, iodides, fluorides, carbonates, silicates, nitrates, nitrites, thiosulfates, and alkali hydroxides. At present the nitrites and nitrates of calcium are the most common inorganic non-chloride accelerators.

Organic Accelerating Admixtures

Triethanolamine is sometimes used to offset the retarding effect of compounds added for other purposes (5,6). Usually the dosage rate of triethanolamine is below 0.5 percent by weight of cement. Above 0.5 percent by weight of cement, strength reduction may occur.

Other organic salts that have been used as accelerators are calcium formates, amine formates, calcium salts of acetate propionate and butyrate, urea, oxalic acid, lactic acid, amine formaldehyde condensates, sodium and calcium thiocyanate (8-14).

The production of ettringite was reported to be greater in mixtures containing calcium formate (8), indicating that it accelerates tricalcium aluminate. Most of the organic salts accelerate tricalcium aluminate.

Effects on Unhardened Concrete

Usually accelerators have a minor effect on workability other than the time available for finishing concrete is reduced. Excessive amounts of some accelerators may cause premature stiffening, and excessive dosage rates of some others may cause retardation.

Temperature is an important parameter. Calcium chloride was reported to have a greater accelerating effect at 0° to 5°C (32° to 41°F) than at 25°C (77°F), (11). Most of the other accelerators would behave in a similar manner.

Bleeding is usually reduced when setting time is decreased. Segregation is not affected by accelerators.

The early heat evolution is increased with calcium chloride and with other accelerators that accelerate the calcium silicates. However, the total heat of hydration at 28 days and beyond is not appreciably affected.

Effects on Hardened Concrete

Strength

Calcium chloride substantially increases compressive strength and flexural strength at early ages (1 and 3 days). The long-term strength is usually unaffected and may sometimes be slightly reduced.

Although the non-chloride accelerators may be effective in decreasing the time of setting, they are typically not as effective as calcium chloride in producing high-early strengths.

Volume Stability

There is some disagreement on the effect that calcium chloride has on drying shrinkage (14). An alternative hypothesis regarding the association of calcium chloride with increased drying shrinkage has been proposed (15). Materials that accelerate calcium silicate hydration may increase shrinkage at early ages, but the long term shrinkage may not be significantly affected.

Durability

Usually accelerators help to produce smaller bubble sizes and smaller spacing factors in air-entrained concrete, which leads to desirable air-void systems. However, the concrete containing the accelerator should be tested according to ASTM C 457 and ASTM C 666 in order to ascertain the air-void parameters and actual resistance to freezing and thawing.

Permeability

Permeability to water is related to the w/c and cementitious material content. For high cementitious content and low w/c, permeability will be low but will increase substantially as cementitious material content is decreased or w/c is increased. Accelerators that adversely affect strength generally increase permeability.

Corrosion

The chloride ions (Cl^-) accelerate corrosion of steel in the presence of oxygen and moisture. Therefore, use of accelerators containing chloride must be avoided or used with great caution in reinforced and prestressed concrete. ACI Committee 222 has determined that the following maximum acid-soluble chloride ion contents should not be exceeded (16).

	<u>Total Maximum Cl^- By Mass of Cement</u>
Prestressed Concrete	0.08%
All Reinforced Concrete	0.20%

All accelerators should be tested to show their effect on corrosion of steel.

Alkali-Silica Reactivity

The expansion produced by alkali-silica reaction is generally greater when calcium chloride is used as an accelerator (17). The effect of non-chloride accelerators should be investigated. The standard ASTM C 227 test method may be used to determine the potential alkali reactivity of cement-aggregate combinations.

Sulfate Resistance

Sulfate resistance of concrete made with non-sulfate-resisting portland cement concrete is reduced when calcium chloride is used. However, when Type V cement was used in concrete of the recommended (ACI 201) low w/c, the addition of calcium chloride did not adversely effect sulfate resistance (17). Non-chloride accelerators should be investigated prior to their use in a high sulfate environment. ASTM C 1012 may be used to determine the length change of hydraulic cement mortars exposed to sulfate solution.

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CHAPTER 5: LATEX ADMIXTURES

General

Polymer modified concrete is an expensive product but can be cost-effective for some highway applications such as thin overlays on bridge decks and other repairs. It is portland cement and aggregate combined at the time of mixing with organic polymers that are dispersed in water. This dispersion is called a latex. The organic polymer is composed of thousands of simple molecules (monomers) that are combined into very large molecules (polymers). In this Chapter, the use of the general description polymer modified applies to both mortar and concrete. The acronyms LMC for concrete, and LMM for mortar, are used where appropriate.

Latexes are added to portland cement mixtures to improve the properties of the final product. These properties include better bond strength, higher flexural strength, better resistance to freezing and thawing, and lower permeability. Additional information about these materials may be found in the State-of-the-Art Report on Polymer Modified Concrete by Committee 548 of the American Concrete Institute (1).

Latex Types

Although many types and formulations of latexes are manufactured, only those developed specifically for use in portland cement are suitable for mortar and concrete applications. The types of latex commonly used are styrene-butadiene, acrylic copolymers, styrene acrylic copolymers, and vinyl acetate ethylene copolymers.

Styrene-butadiene is the most commonly used latex for concrete overlays on bridge decks and to date is the only one that has been evaluated for such overlays by the Federal Highway Administration (2). In addition to styrene-butadiene, other latexes are used in mortar applications, such as patching, floor leveling, tile grout and adhesive, stucco, and the like.

Mechanism of Latex Modification

The mechanism of latex modification of portland cement involves two processes: the hydration of the

cement and coalescence of the latex. The chemical reactions of cement hydration occur the same as in conventional mortar and concrete. While this is taking place, water is being consumed and removed from the latex dispersion, concentrating the latex particles and bringing them closer together. With continual removal of water, both by cement hydration and evaporation, the latex particles eventually coalesce into a polymer which is interwoven throughout the hydrated cement particles and which coats these particles and the aggregate surfaces with a semi continuous plastic film. This results in partially filled void spaces, as well as good adhesion between the aggregate and cement hydrate.

Mixture Proportions

Materials

Mortar and concrete incorporating latex consist of portland cement, aggregate, latex, water, and possibly other chemical admixtures. The selection of the specific aggregates is normally dependent on the thickness of the application, just as in conventional mixtures.

The portland cement used in latex-modified mixtures is usually Type I or Type II. However, when early strength is required, Type III may be used. For mortar applications where color is important, white cement is used, in conjunction with the acrylic or vinyl acetate latexes.

The aggregate requirements for latex mixtures are similar to those for any quality mortar or concrete mixtures, i.e., they should be clean and sound and of an industry standard grading suitable for the application.

The choice of latex will depend on the application. For concrete, styrene-butadiene has been most often used.

AE and water reducers are not needed with these mixtures. For some mortar applications, workability additives, such as methyl cellulose, are used.

Mortar Proportions

LMM consists of cement and fine aggregate at ratios ranging from 1/2 to 1/5, depending on the

end use. Because most latex formulations function as water reducers, a w/c of less than 0.40 is common, with the water in the latex being included in this ratio. Since latexes are water dispersions, it is important to know the latex solid content of a particular product before designing the mixture. Knowing this, the amount of latex liquid required can be determined, based on a specified latex solids-cement ratio. Frequently this is 0.15.

Concrete Proportions

Mixture proportioning parameters for concrete made with latex are similar to those for mortars incorporating latex as given above. Cement is usually Type I or Type II, although some special needs have been met by using Type III. A cement factor of 7 bags/yd³ is typical; latex content is 24.5 gallons/yd³. There is typically more fine aggregate than coarse aggregate since overlays, the typical end use, require some amount of texturizing for skid resistance. Good workability at low w/c (less than 0.40) with slumps of 4 to 7 inches are normal for LMC and result from the latex formulation. Usually no more than 6.5 percent air is entrained by the latex.

Properties of Unhardened Concrete

The properties of unhardened LMC include good workability at low w/c and air contents of 3 to 6.5 percent. However, the finishing characteristics are normally described as increasing drag or stickiness on the finishing tool. Also, if the exposed surface is allowed to dry it forms a thin crust (approximately 1/16 in. thick) which may be difficult to finish.

Properties of Hardened Concrete

The addition of latex to mortar and concrete mixtures will usually result in increased bond, tensile, and flexural strength, but no significant change in compressive strength (3,4,5). Permeability to liquids and gases is significantly decreased; resistance to freezing and thawing will be increased (6).

Mortar Applications

LMM is generally used where good adhesion of relatively thin sections is required. Typical

applications include use as concrete floor leveling material, adhesive for ceramic tile, and stucco.

Concrete Applications

The most widespread use of LMC has been as an overlay on bridge decks (7). These typically have been 1-1/4 in to 2 inches thick, and have been applied to new construction, as well as repair and rehabilitation projects. The function of these overlays has been to provide a well bonded, long-wearing riding surface that also functions as a barrier to deicing salts. To a lesser extent but for the same reasons, LMC overlays have been used in parking garages.

Limitations

As with conventional portland cement, these materials should be used with caution during extreme weather conditions. At low temperatures (i.e., 40°F) some latexes will not cure properly. At high temperatures (i.e., 85°F) rapid setting can occur. During conditions of rapid drying (i.e., high wind and low humidity), latex systems are more sensitive to plastic shrinkage cracking than conventional mortars and concrete, because of the film-forming characteristics of the latex. This will cause a skin (or crust) to form if the surface is allowed to dry. Therefore, when ambient conditions create an environment for rapid evaporation, measures should be taken to protect the concrete surface from rapid drying.

Since LMM and LMC require air drying to achieve their optimum properties, these systems are not suitable for underwater applications unless sufficient time is allowed for drying. This can be monitored by curing samples under identical conditions as the field installation and testing the samples periodically until the design strengths are achieved.

For exterior applications, or where exposure to moisture is likely, polyvinyl acetate (PVA) latex should not be used since it will hydrolyze into a water-soluble form. There is concern about using PVA latex in any highway application because its physical properties are poorer than the other available latexes (8).

Guidelines and Specifications

At present, there are no standard ASTM or AASHTO specifications for LMC. However, the state-of-the-art report prepared by ACI Committee 548 provides additional information about the properties of polymer modified concrete and includes special specifications and guidelines for the use of this material.

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CHAPTER 6: CORROSION-INHIBITING ADMIXTURES

General

This class of admixture provides protection for ferrous materials embedded in concrete by reducing the corrosion rate in the presence of chloride ions. Inhibitors act at the steel surface to limit either the anodic or the cathodic electrochemical reaction involved in the corrosion process, and in some cases could prevent chloride ions from reacting at the surface. It has also been observed that some corrosion-inhibiting admixtures inhibit the corrosion of aluminum and galvanized steel in concrete (1).

Reaction with Portland Cement

The exact mechanism of reaction of corrosion inhibiting admixtures are not well defined. Depending upon their composition, various theories postulate that they: (a) react with the tricalcium aluminate component of cement to form monosulfoaluminate-like or ettringite-like compounds; or (b) accelerate or retard the hydration of the tricalcium silicate of cement.

Chemical Composition

Salts such as benzoates, chromates, and nitrites are known to be corrosion inhibitors. Only calcium nitrite has been shown to be nondetrimental to the mechanical properties of concrete (2,3).

Reaction Mechanism of Corrosion Inhibitors

In alkaline environments, such as concrete, a natural iron oxide forms on the surface of the steel. This oxide layer consists of two types of oxides -- ferrous oxide and ferric oxide. Ferrous oxides, though stable in alkaline environments, will react with chloride ions to form complexes that move away from the steel to form rust. The chloride ions are released to attack the steel again. Eventually, the entire passivating oxide layer is undermined. It is theorized that anodic inhibitors, such as nitrites, help to promote the formation of the protective ferric oxide

layer that is resistant to the attack by chloride ions, thus inhibiting the corrosion.

Effect on Unhardened Concrete

Alkali metals and alkaline earth salts of benzoic and chromic acids generally retard the time of setting of concrete. Chromate can also cause discoloration of the concrete. Nitrites are accelerators. This effect may be offset by the use of retarding admixtures. Some of the salts might require changes in air-entraining admixtures dosages for a given level of air entrainment.

Effect on Hardened Concrete

Alkali metal and alkaline earth salts of benzoic acid and chromic acid reduce the ultimate compressive and flexural strengths of concrete. Calcium nitrite usually increases the ultimate compressive and flexural strengths of concrete.

Addition Rate

The known corrosion inhibitors are added to concrete at a rate of 1 to 3 percent solids by mass of cement. In warm weather, a retarding admixture is usually added to offset the acceleration of the time of setting when a nitrite-based corrosion inhibitor is used.

Precautions on Use

Research on sodium nitrite, potassium chromate, and sodium benzoate (4) indicate that these compounds should not be incorporated into concrete as a corrosion inhibitor. Because of the relatively large addition rates required for corrosion protection, sodium and potassium salts of benzoic, chromic, and nitrous acids tend to aggravate any potential alkali-aggregate reaction which causes expansive disruption of the concrete (2). These same salts also reduce the strength of concrete (5,6). As indicated earlier, calcium nitrite, has been found to be nondetrimental to the mechanical properties of concrete (2,3).

Compatibility

Corrosion inhibitors are compatible with other admixtures in concrete, but they should not be mixed with other admixtures prior to their addition to concrete. They can be added to concrete at either the batch plant or the job site. Chromates are toxic, therefore, requiring special precautions when being handled.

Methods of Measuring Effectiveness

Electrochemical corrosion monitoring techniques are commonly and effectively used in laboratories to measure the corrosion of metal embedded in concrete. The most common, yet least accurate, method is the use of copper-copper sulfate half-cells to measure corrosion potentials (ASTM C 876).

Other techniques including polarization resistance, linear polarization and electrochemical impedance are also used, and descriptions of these techniques are readily available. Macrocell corrosion tests measure galvanic corrosion between the upper mat of rebar (exposed to chloride ions) and the lower mat, which is presumably not corroding (7-13).

Specifications

A standard method of test for rapid determination of corrosion inhibiting properties of chemical admixtures for concrete is under consideration by ASTM. A similar test is also being considered by AASHTO.

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CHAPTER 7: POZZOLANS

General

A pozzolan is defined as a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form hydrated compounds possessing cementitious properties. Pozzolans can be classified into two groups: (a) raw or calcined (heated to alter composition) natural pozzolans, and (b) artificial pozzolans.

Natural pozzolans include finely ground diatomaceous earths, opaline cherts and shales, tuffs, and volcanic ashes or pumicites. Some of the natural materials may require calcination to develop suitable pozzolanic properties. Natural pozzolans are used primarily in concrete for massive structures such as dams where limitation on temperature rise during hydration is of primary concern. Natural pozzolans, classified by ASTM C618 as Class N, are seldom used in highway construction, and thus will not be discussed further in this report.

Artificial pozzolans include fly ash (the finely divided by-product from burning powdered coal), and silica fume (the extremely fine by-product of the manufacture of silicon metal and ferrosilicon alloys).

ASTM C 618 classifies fly ash as Classes F and C (1).

The separation of fly ash into two classes reflects differences in chemical composition resulting from the types of coal burned. The Class F fly ashes are derived from anthracite or bituminous coals and are primarily pozzolanic with little or no self-hardening properties in the presence of water only. The Class C fly ashes are derived from sub-bituminous coal or lignite, and some have cementitious properties in addition to pozzolanic properties. It should be noted that some products from sub-bituminous coals will also meet the ASTM requirements of Type F fly ash.

The use of silica fume in the United States is relatively recent. As of 1989, ASTM and AASHTO are considering, but have not adopted, standard specifications for silica fume.

Ground granulated iron blast-furnace slag used as

a cementitious ingredient in concrete is not a pozzolan but a latent hydraulic cement. Slags are discussed in Chapter 8 of this report.

The amounts of pozzolan used and the purpose for its use in concrete for construction of pavements or other transportation facilities vary depending on the type of material. Each material will be discussed separately in the following sections.

Fly Ash

When used in concrete, fly ash generally contributes to the strength gain and improves concrete durability. The fly ash may be added either as a replacement for a portion of the portland cement or as an addition to the usual amount of cement. The method of use will depend on the primary consideration which may be to reduce costs or to impart special beneficial properties to the concrete as will be discussed.

Considerable literature exists concerning the use of fly ash in concrete, including a number of summaries and state-of-the-art reports (2,3). However, it is important to note that all the literature on fly ash prior to 1970 makes no reference to Class F or Class C. At that time, the only product available was from anthracite or bituminous coal which is now designated as Class F. Findings in early research based on the Class F fly ashes may not be applicable to Class C fly ashes.

Class C fly ashes are derived from burning subbituminous coal. Some Class C fly ashes have substantial amounts of calcium compounds which impart significant self-hardening properties. These compounds, usually a form of calcium silicate, hydrate and harden when water is added in much the same way as portland cement, leading to early strength contribution. Most Class C fly ashes also have substantial amounts of pozzolanic components that add further strength by reacting with the lime from cement hydration as it becomes available.

The following sections emphasize the factors relating to the use of either type of fly ash in concrete for highway and bridge applications, the potential benefits, and the possible problems that might arise.

Specifications

In the United States, the most often used specifications for fly ash are ASTM C 618 and AASHTO M 295. While some differences exist, these two specifications are essentially equivalent. Some state transportation agencies have specifications that differ from the standards. The major differences in requirements relate to magnesium oxide (MgO) content or the pozzolanic activity test.

Quality Assurance Procedures for Fly Ash

Complete testing of fly ash for compliance to all specification requirements is time consuming and impractical for individual shipments of fly ash to a job site. Thus, it is customary for user agencies to evaluate the suitability of a source and accept individual shipments of fly ash on the basis of certification and possibly tests for fineness (passing 45 μm (No. 325) sieve) and loss on ignition which closely approximates the carbon content of the fly ash.

All fly ashes are not suitable for use as a pozzolan in concrete. The source of the coal, burning conditions, and possibly the method of handling after collection all can affect the fly ash quality as a pozzolan. The use of certain additives to aid precipitation also negates the value of the fly ash as a pozzolan. However, at the present time most fly ash marketers screen their materials for suitability and maintain their own quality control standards. They will certify continuing compliance with ASTM C 618 requirements. In general, those agencies using certification procedures have had satisfactory results.

Mixture Proportions for Fly Ash Concrete

ACI Standard Practice 211.1 provides general guidelines for establishing the mixture proportions for concrete using pozzolans (4). As stated there, a water-to-cement-plus-pozzolan ratio $[w/(c+p)]$ by mass must be considered in place of the traditional water-to-cement ratio (w/c) by mass. Replacement may be by either an equivalent mass or volume.

Most highway agencies use mass equivalency and establish the requirement that the maximum $w/(c+p)$ is equal to the maximum w/c normally specified for the same class of concrete using portland cement only. The maximum proportions of

the cement that can be replaced by the fly ash are specified, and the minimum mass of cement plus pozzolan is set at the same value as the initial mass of portland cement. Some agencies also specify that a larger mass of fly ash than that of cement replaced be added.

Requirements for the 28-day strength for fly ash concrete are the same as the requirements for the same class of portland cement concrete.

These established limiting values should not automatically be used as the proportions for the fly ash concrete. Variations in the water requirements for a designated slump will occur because of the quantity, type, and fineness of the fly ash, and fly ashes will interact differently with different cements. Thus, for best results, trial mixtures should be made of the fly ash concrete using the same source of materials to be used in the job.

Effects on Unhardened Concrete

Air Entrainment. When fly ash is used, the amount of air entrainment (AE) required to obtain a given air content is expected to increase. The amount of the increase depends on the fly ash being used. For example, a Class C fly ash with a low loss on ignition may require virtually no AE adjustment, whereas a Class F fly ash with a high loss on ignition may require two or three times the dosage rate of AE as the reference concrete. The increase in AE is ordinarily caused by: (a) the larger amount of cementitious material that is present; (b) an increase in the surface area due to the overall greater fineness of the particles in the mixture; and (c) the presence of free carbon or other organic materials that may partially adsorb the admixture (2).

Because of the known tendency of some combinations of cement, fine aggregate, fly ash, and AE to rapidly lose entrained air during transit of the concrete, the percentage of entrained air should be monitored closely at the job site.

Water Requirement. The effect of fly ash on the water requirement of concrete depends on the mixture proportions and the fineness and shape of the fly ash particle. These have counteracting effects. Increased fineness tends to increase the water demand of the concrete for a given slump, but the spherical particle shape of the fly ash provides for lower internal friction so that the net change

may be only a slight change in water requirement. In those mixtures where cement content is reduced to take advantage of the pozzolanic properties of the fly ash, the required water content of the concrete for equal slump may be less than that of non-fly ash mixture.

Workability and Finishing. The addition of a suitable fly ash to concrete mixtures will usually improve workability. This improvement results from the additional fine material that increases the surface area of the solids per unit of water volume enabling a reduction in particle interference. The spherical particle shape of fly ash also provides increased workability because of the "ball-bearing" effect. The improvement in workability is more pronounced when pozzolan is added as a replacement for part of the fine aggregate rather than as a replacement for cement.

However, some situations are encountered when the addition of fly ash results in stickiness and consequent difficulties in finishing. In such cases, the mixture may have too much fine material or the air content may be too high and corrective action must be taken. It is suggested that the entrained air content first be checked and brought back into compliance if necessary. If the problem persists, the mixture should be examined from the standpoint of reducing the total fines present. However, in situations where the fly ash is being added to protect the concrete from the harmful effects of chemical attack (such as sulfate), it may not be possible to reduce the pozzolan content without negating the desired effect. In such cases, a reduction in the fine-to-total aggregate ratio or a change in the source of fine aggregate to provide coarser material may be needed to eliminate the problem.

Fly ash concrete typically has a longer time of setting and may require finishing at a later time compared to mixtures without fly ash. Too early finishing may seal bleed water under the top surface. This would create a plane of weakness in the hardened concrete.

Bleeding. Fly ash mixtures normally have a lower rate of bleeding than comparable concretes without fly ash, because the ratio of surface area of solids to the volumes of water has been increased and the paste is less watery and less inclined to separate.

Time of Setting. The effects of fly ash on the time of setting depends on the characteristics and amounts of fly ash used. All Class F fly ashes generally increase the time of setting as do most Class C materials. However, some Class C fly ashes reduce the time of setting, most likely because of their own cementitious qualities.

For highway construction, changes in the time of setting of fly ash concrete compared to concrete without fly ash usually will not introduce a need for changes in construction techniques and the delays that occur are often advantageous. However, delays up to four hours have been observed with some mixtures; thus trial tests should be made with the actual mixture proportions and materials for the job before the start of field placements.

It should also be recognized that pressures on form work may be increased because of the slower slump loss and retarded setting characteristics (2,3). In addition, longer times of setting may increase the chances of plastic shrinkage cracking, especially when high evaporation rates occur.

Effects on Hardened Concrete

Strength. Strength of fly ash concrete and the rate of strength gain are affected by the characteristics and the amounts of the particular fly ash, and the cement with which it is used. Also, longer curing periods than those required for concretes without fly ash may be needed to obtain the full benefits of the pozzolanic properties of the fly ash. The temperature existing during the placement and curing period also affects the concrete properties, especially at early ages. In warm weather the pozzolanic reaction is accelerated and faster strength gain is expected. In cold weather the strength gain in fly ash concretes can be more adversely affected than the portland cement concretes; therefore necessary precautions must be taken such as those described in ACI 306 on cold-weather concrete.

Normally, all fly ash concretes proportioned to have 28-day compressive strengths equivalent to similar concrete without fly ash will have greater ultimate strengths when properly cured. However, such concretes containing a typical Class F fly ash usually have lower strength at 7 or fewer days of age than the equivalent non-fly ash concrete. High strengths at early ages equivalent to non-fly ash concrete can be attained in fly ash concrete by use

of accelerators or adjusting the mixture proportions, for example, lower water to cementitious material ratios with water reducers.

Class C fly ashes with significant cementitious properties may develop equivalent or greater strengths than similar concrete without fly ash at early ages.

Resistance to Freezing and Thawing. The effects of fly ash and other pozzolans on the resistance of concrete to freezing and thawing and to the actions of deicing chemicals depend on the adequacy of air entrainment, the strength or maturity of the concrete, and its moisture condition at the time of exposure. Data obtained from freezing and thawing of adequately air-entrained concrete with cement as the only cementitious material and with other mixtures containing fly ash as part of the cementitious constituent show that, regardless of age or the w/c ratio, the resistance to freezing and thawing will be adequate if the air-void system of the paste is proper, the aggregate is sound, and the concrete is not allowed to undergo cycles of freezing and thawing in a critically saturated state until it has developed a compressive strength of 4,000 psi or greater (5). Fly ash concrete may exhibit somewhat higher surface scaling in the presence of deicers, especially at early ages. However, such scaling is limited to the top surface and does not affect the internal structure and the integrity of the concrete (3).

Permeability. When concrete is used for pavements and bridges, the major concern is the resistance of the concrete to penetration by chloride ions or other aggressive fluids. The characteristic referred to as chloride ion permeability is usually assumed to be closely related to the permeability of concrete to water.

The use of fly ash tends to reduce the permeability of the concrete and thus retards the infiltration of aggressive liquids. Accordingly, better resistance to corrosion of embedded metals is provided as compared to non-fly ash concrete.

The permeability of fly ash concrete generally decreases with time because of the pozzolanic reactions that occur after the concrete has hardened. The amount of decrease is dependent on good curing practice and the temperature at which curing occurs. Laboratory tests have indicated that significant reduction in permeability of fly ash

concrete to the chloride ion (as determined by AASHTO Test T 277) is attained by curing specimens at 100°F in lieu of 73°F, thus indicating the advantage of placing fly ash concrete in hot summer weather (6). Conversely, placement in cold weather may have adverse effects on the permeability.

Alkali-Silica Reactivity. When used in sufficient quantity, fly ash is capable of preventing excessive expansion resulting from the alkali-silica reaction (2,3). The alkali-silica reaction produces expansion by the formation, after hardening, of a gel that can absorb water and swell. Fly ash and other pozzolans effectively prevent the formation of the expansive gel by early reaction with the alkalis present to form a non-expansive calcium-alkali silicate. Thus, the hydroxyl ions remaining in solution are insufficient to react with the aggregate particle. However, if used in too low an amount, fly ash may not be effective, and it can even be detrimental under some circumstances (7).

Sulfate Resistance. As a general rule, Class F fly ash will improve the sulfate resistance of mixtures in which it is included. However, Class C fly ashes containing a high ratio of calcium to iron oxides or those with large amounts of chemically active alumina may lower sulfate resistance. Thus, where maximum sulfate resistance is needed, fly ash with a known performance relative to sulfate resistance should be selected, along with cements that have good performance records in a sulfate environment.

Temperature Rise. Concrete containing Class F fly ash develops less heat per unit of time than similar concrete without fly ash. Therefore, the temperature rise in large masses of concrete such as large foundations or piers for bridges is significantly reduced. Accordingly, lower thermal stresses are encountered as the mass cools, and the danger of cracking is reduced. The pozzolanic reactions also provide added strength that aid in counteracting thermal stresses. While some Class C fly ashes may also decrease temperature rise, those materials with significant cementitious components that react quickly may contribute to a greater temperature rise. Therefore, when Class C fly ash is used and heat of hydration is of critical concern, the proposed concrete mixture should be tested for heat of hydration performance.

Because the rate of strength gain of fly ash concrete may be affected by temperature to a greater extent than similar concrete without fly ash, precautions must be taken if fly ash concrete is to be placed in cold weather. Greater delays in removing forms or allowing traffic on pavements may be necessary. Conversely, there is evidence that in hot weather, fly ash concrete is not adversely affected by the increased curing temperature conditions as is concrete without fly ash (6).

Handling

Storage. Fly ash should be stored in separate weather-tight silos much the same as cement. Common-walled bins for cement and fly ash are to be avoided if at all possible. If common-walled bins are necessary, the common wall must be of double construction with air space between the two partitions and with "weep holes" at the bottom so that failure of a partition can be detected.

Fly ash and cement silos should also have their own separate dust collectors. Under no conditions should the dust collectors mounted on the cement silo be used to vent the fly ash silo.

Delivery transport pipes for fly ash should be kept as far as possible from such pipes for cement, and all should be plainly marked with signs clearly indicating the product being delivered. As a further safeguard, it is suggested that the delivery pipes be equipped with locking dust caps and that the keys to them remain in the custody of the plant superintendent.

Batching. Fly ash may be transported from the point of collection to the batcher with the some of the same kinds of equipment used to transport cement. Gravity, air slides, and screw conveyers are satisfactory, provided a positive shut-off valve is used. The shut-off valve is necessary because the spherical particle shape and fineness of fly ash allows it to flow easily. Aerated fly ash will flow like water and has been known to flow upward through inclined screws. To facilitate fly ash movement, it is suggested that fly ash bins be well-aerated by means of low-pressure, air-diffusing pads.

Fly ash should be dispensed by mass into the concrete batch. If it is weighed cumulatively in the same batcher or on the same scale, it should be weighed after the cement. As a further precaution,

electronic safeguards can be installed to prevent the fly ash valve from opening until the cement valve has closed. For best results, the fly ash should be introduced into the batch along with all of the other concrete-making materials.

Introduction of dry fly ash into concrete which has already achieved some measure of homogeneity (especially in transit-mix operations) often results in unmixed fly ash in excessive quantities at the back of the truck mixer and no fly ash at the front of the mixer. Frequently, balls and pellets of fly ash are formed by the addition of dry fly ash to already mixed concrete.

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Silica Fume

General

Silica fume is the fine pozzolan obtained as a by-product of the manufacture of silicon or silicon alloys, such as ferrosilicon. Silica fume has also been referred to as "condensed silica fume" or "microsilica." Although the product has been studied since the early 1950s (1), reliable supplies of silica fume and silica fume-based admixtures have been available to the concrete industry only since the late 1970s. Silica fume is appreciably more expensive than portland cement, but its use can be cost-effective. Its use in the transportation field is advantageous for specialized applications as in overlays or high-strength concrete columns.

Silica fume typically is collected from the exhausts of electric furnaces producing silicon or ferrosilicon alloys that have silicon contents of 75 percent or more. Exhaust fumes from the furnaces are cooled and passed through fiber filters. The particles are then deposited into hoppers. This dry product may either be used directly, or it may be processed to increase the silica (SiO_2) content by removing impurities and large particles.

Silica fume admixtures for concrete are furnished either in the dry form or as water-based slurries that are made from dry material.

Physical Properties

Silica fume is gray, and is darker with increasing carbon content. The product is very finely divided, with most of the particles being in the 0.1 to 0.2 micrometer range, which is about 1/100 of the diameter of the average sized cement particle. The specific surface as measured by nitrogen absorption methods (the Blaine air permeability test is not appropriate) usually ranges from 13 m^2/g to 28 m^2/g with the surface area of silica fume used in concrete admixtures generally lying in the middle of this range. Material retained on a 45 μm (No. 325) sieve is commonly referred to as oversize. Oversize material is mostly foreign matter such as rust, wood chips, coal, and coke. Generally, the percentage of oversize in the product as collected is well under 6 percent, although the current Canadian standard allows a maximum of 10 percent (2).

The specific gravity of silica fume suitable for use in concrete generally ranges from 2.2 to 2.3. Loose

bulk densities of undensified silica fumes range from 5 to 27 pounds per cubic foot (pcf). Silica fumes intended for use in concrete are generally in the middle of this range as produced. Densified silica fumes generally have loose bulk densities ranging from 25 to 40 pcf (3).

Chemical Properties

The principal ingredient of silica fume is silica (SiO_2), which is in the non-crystalline (amorphous) state. Generally, silica fumes that are used in concrete admixtures have silica contents exceeding 85 percent. The second most abundant constituent found in commonly-used silica fumes is carbon, which is the unburned residue from the smelting process. Fe_2O_3 content may be as high as 1 or 2 percent, but other oxides, Al_2O_3 , CaO , MgO are usually present in percentages of less than 1 percent (5).

Since 85 to 95 percent of the loss on ignition (L.O.I) results from the burning of the carbon, the L.O.I. test is generally used as a measure of this constituent. L.O.I. varies, and the maximum value set by the Canadian standards is 6 percent.

The moisture content of dry collected silica fume is very low. Although the Canadian standard allows a maximum of 3 percent, products will normally have only about one-tenth of this amount.

The viscosity and gelling tendency of slurried silica fume admixtures may be related to the pH of the slurry. However, no association between pH and concrete performance has been demonstrated for typical silica fume dosages (4 to 20 percent of the cement by mass).

Silica Fume Products

Silica Fume is commonly supplied in several forms. These are described below.

Undensified. Undensified silica fume (as it comes from the furnace) is difficult to handle: it tends to lump during shipping; it may cake during extended storage; and it is associated with significant dust levels. Although undensified silica fume may work well in concrete, transportation costs beyond about a 100-mile radius from the silica fume source are usually prohibitive because of the low loose bulk density.

Undensified silica fume is sometimes used to make blended cement. Nearly all cement used in Iceland contains 7-1/2 percent of 75 percent ferosilicon silica fume (6), and some cements in Canada also have been blended with low amounts of silica fume (3).

When undensified silica fume is used in various blended bagged products, high shipping costs may be justified.

Densified. To overcome the relatively high transportation costs, silica fume may be densified. Densification improves the handling characteristics of silica fume and reduces significantly the amount of dust generated during handling and dispensing. Densified products generally have a loose bulk density in the 25-40 pcf range. For each silica fume source, there is a loose bulk density value beyond which the particles fail to crumble and disperse efficiently in concrete.

Densified Formulated. Dry water-reducing admixtures, usually ASTM C 494 Type A and/or Type F admixture, are added to densified silica fume to produce dry formulated products. Such a product may also contain up to 5 percent portland cement. The formulated densified products tend to possess strong water-reducing properties in concrete. The handling and dusting characteristics are essentially the same as for densified silica fume.

Pelletized. Pelletized silica fume has been densified beyond the point where the particles can disperse in concrete to any useful degree. The most common reason for pelletizing silica fume is to prepare the material for disposal, usually in a landfill. Pelletizing not only enables the efficient use of landfill space, but it also reduces significantly the contamination of water resources around the landfill (3).

Usually pelletized silica fume is prepared by adding water to undensified or densified silica fume on large disk pelletizers. Apparently soluble portions of silica fume glue particles together more or less permanently upon subsequent drying. In some cases cement is used as a binder. In at least one instance, crushed pelletized silica fume has been used to produce blended cement (3).

Slurried. Undensified silica fume may be blended with water to make a nominal 50 percent silica fume-50 percent water slurry, which is sometimes

referred to as plain slurry. This enables transportation costs to be reduced significantly relative to undensified silica fume, because over twice as much solid material is contained in a cubic foot of slurry (37-43 pcf of silica fume) than in a cubic foot of undensified silica fume (typically 16 pcf).

Advantages of the slurried silica fume include being able to blend many days and weeks of production into large tanks to improve product uniformity. Oversize particles are easily removed by screening, and slurried products may be dispensed accurately. Slurried products must be protected from freezing and evaporation.

Slurried Formulated. As with densified silica fume, chemical admixtures may be added to slurry to produce formulated products. These essentially have the same handling characteristics, advantages, and disadvantages of plain slurry.

Formulated slurried products are available in Europe, North America, Japan, and Chile. Most of these products contain enough chemical admixtures to either counteract the otherwise increased water demand caused by silica fume or to actually reduce significantly the water requirement of concrete.

Specifications

No national ASTM or AASHTO standard has yet been adopted, although an ASTM specification is being developed. However, a Canadian national standard does exist, as well as standards for a number of European countries, including Denmark, Finland, Norway, Sweden, and the United Kingdom. The American Concrete Institute is currently developing a summary of information on silica fume.

Quality Assurance Procedures for Silica Fume

At the present time, quality is dictated by job specifications that list acceptable limits or ranges for various silica fume properties. Some silica fume suppliers maintain internal quality standards, which tend to be geared toward satisfying customer needs. In general, agencies requiring certification procedures have seen satisfactory results.

Mixture Proportions for Silica Fume Concrete

Silica fume suppliers and experienced silica fume concrete producers are the best sources of information regarding the development of trial batches. It is best to demonstrate acceptable performance through a trial batch process using the materials, procedures, and exposure conditions that will be experienced on the job.

In the United States, existing portland cement concrete mixtures are usually modified with additions of silica fume, while in Canada it is common to use silica fume on a cement-replacement basis. Silica fume dosages for most applications generally range between 3.8 percent and 20 percent of the cement, by mass. The largest volume of concrete will have silica fume contents between 5 and 10 percent by mass of cement.

In many cases the silica fume is considered to be cementitious material, and it is included in the water-to-cementitious materials ratio $[(w/(c + sf))]$ determination. Regardless of whether or not the silica fume is included in the $w/(c + sf)$ calculation, this point should be agreed upon prior to work proceeding on a project. Similarly, whether the silica fume is used as an addition to or as a replacement of the cement should be stated in the job specification. Because silica fume itself has a positive water demand, it is nearly always used with water-reducing chemical admixtures. The formulated silica fume products lessen the amount of separately-added admixtures that may be needed in a mixture.

Silica fume has been used successfully with other pozzolanic materials, such as Class C fly ash, Class F fly ash, and ground granulated iron blast-furnace slag.

Effects on Unhardened Concrete

Air Entrainment and the Air-Void System. It is possible to entrain a desired amount of air in silica fume concrete using commercially available air-entraining admixtures (AE) that have shown acceptable performance with the same materials. However, occasionally, the AE dosage may need adjustment. Usually, a small increase is needed, although in many cases no change is indicated. Less frequently a small decrease is required. Whenever possible, the AE dosage for a mixture should be

determined using a full-scale trial batch. Thereafter, the AE dosage for a mixture will be affected by the same factors that affect the required AE dosage for portland cement concrete.

It is possible to achieve acceptable air-void systems for frost-resistant concrete. However, the presence of HRWR (high-range water-reducing admixtures) may lead to coarser air bubbles (7).

Water Requirement. Silica fume added to concrete by itself increases water demand, often requiring an additional pound of water for every pound of added silica fume to maintain constant slump. Therefore, silica fume is nearly always used in conjunction with relatively high dosages of water-reducing admixtures or HRWR. As previously mentioned, some of the commercially available formulated silica fume products exhibit water-reducing properties.

Workability, Cohesion, Bleeding, and Finishing. Primarily because of increased cohesion, silica fume concrete generally requires somewhat higher slump (by one to two inches) to achieve workability similar to portland cement concrete. As cohesion is increased, the risk of segregation is decreased. Thus, in mixtures with silica fume, high slump is usually tolerable.

Generally, increasing silica fume content is associated with increasing adhesion (stickiness), although low-dosage silica fume concrete may not be much different from portland cement concrete. Fortunately, at the silica fume dosages commonly used in ready-mixed concrete, equipment and tools can still be cleaned adequately with water.

Beyond about 5 percent silica fume dose, the stickiness of the concrete to magnesium and wooden tools has led some finishers to also employ steel tools. Vibratory screeds are recommended for consolidating and leveling the surface; however, successful completion of a finish may require changes in the tools used and in the time of operations.

The increased stickiness makes silica fume ideal for incorporation into shotcrete (both dry and wet methods). Here, adding silica fume to the mixture improves bond and significantly reduces rebound.

Some engineers take advantage of the non-bleeding characteristics of silica fume concrete by specifying finishes that may be applied immediately after screeding and initial finishing. These may include tined, broomed, and

burlap-dragged finishes. Curing may usually begin immediately, thereby eliminating the risk of plastic shrinkage cracking. This approach may also reduce finishing costs. The greatly reduced bleeding tendency of most silica fume concrete makes it important for contractors to adhere to good concrete practice when plastic shrinkage cracking may be a concern. This means that when the weather conditions warrant, precautions against plastic shrinkage cracking should be taken. Common protective methods include appropriate use of misters, applying evaporation inhibitors, delaying placement for better weather, and beginning curing at the earliest appropriate moment.

The cohesiveness of silica fume concrete makes it ideal for use in underwater concrete applications. Underwater placements of silica fume concrete in the United States began in 1988.

Time of Setting. Silica fume itself has no significant effect upon time of setting of concrete as determined by ASTM C 403. However, silica fume is nearly always used in conjunction with chemical admixtures that affect the time of setting of silica fume concrete in the same manner that they affect portland cement concrete. Also, temperature affects the time of setting of silica fume concrete and portland cement concrete similarly.

In some cases the surface of silica fume concrete may appear dry and ready for final finishing; however, the concrete below the surface may still be insufficiently hardened to support the weight of finishers and equipment. This condition may be alleviated by the same measures that are used to prevent plastic shrinkage cracking.

Effects on Hardened Concrete

Strength. Other factors being equal, addition of silica fume to concrete increases strength. Also, incorporation of silica fume into a mixture with HRWR enables the use of lower water-to-cementitious materials ratio than may have been possible otherwise. Compressive strengths between 6,000 psi and 12,000 psi have been used in bridges (8,9,10), and an air-entrained silica fume concrete mixture developing strength of 15,500 psi at 56 days has been reported (3). Compressive strengths between 9,000 psi (11) and 12,000 psi (12,13) have been specified for high-rise buildings. Strengths around 20,000 psi were achieved in some cases (14).

Some bank-vault manufacturers use silica fume concrete that achieves over 18,000 psi at 28 days (15), and compressive strength as high as 38,910 psi has been reported for a silica-fume-modified portland cement-based mortar (16). The existence of 20,000 psi proprietary silica-fume-modified mortar mixtures has been reported (3).

Silica fume concrete has been shown to improve the early age strengths of concrete using fly ash or granulated blast-furnace slag (17,18,19). Various departments of transportation have used silica fume to achieve high-early strengths for bridge decks and bridge piers (8). Eighteen-hour strengths between 3,000 psi and 7,000 psi have been reported for silica fume concrete used in precast elements (11).

The modulus of rupture of silica fume concrete is usually either about the same as or somewhat higher than that of portland cement concrete when compared at the same compressive strength level (20,21). The splitting tensile strength of silica fume concrete generally follows the same relationship to compressive strength as portland cement concrete (21).

The bond strength of silica-fume-modified paste to aggregate is significantly increased even when low or moderate silica fume dosages (5 percent - 10 percent) are used (22,23). Various studies have demonstrated that reinforcement fiber-to-concrete (24,25) and concrete-to-concrete (26) bond strength is increased.

Resistance to Freezing and Thawing. It has been found that the traditionally acceptable values for the spacing factor, (0.008 in. or less), and the specific surface, (600 in²/in³ or more) apply to silica fume concrete. However, in general, silica fume concretes, with HRWR having marginal air-void systems by the usual standards show acceptable resistance to freezing and thawing since it is difficult to critically saturate these concretes (3,7,15,21).

Permeability. Addition of silica fume to concrete reduces the water permeability by at least one order of magnitude (27), and in many cases the permeability is so low that existing equipment is not suitable for measuring the permeability of silica fume concrete (27,28).

Low water permeability also results in greatly increased resistance to the penetration of chloride ions, and adequate resistance for concretes used in highway application may be attained with relatively

low silica fume dosages (5 to 7.5 percent). Achieving low permeability represents one of the primary reasons why silica fume concrete is used in bridges, parking garages, and marine structures (7,8,9,10).

Electrical Resistivity. Addition of silica fume to concrete increases electrical resistivity significantly. This reduces corrosion current in concrete and thereby slows the corrosion of steel in concrete. One report indicated that electrical resistivity was increased (improved) by a factor of around 16 when a 20 percent silica fume dose was used (29). Various unpublished information, often employing the AASHTO T 277 test, has shown improvement factors ranging between 20 and 50 at the 20 percent dose. Improvement factors between three and eight have been seen at the 5 percent dose, again from unpublished information.

Chemical Resistance. Relatively large dosages of silica fume, in the 12 to 20 percent range, are usually employed for chemical-resistant applications. This is done to reduce the $\text{Ca}(\text{OH})_2$ content in the silica fume concrete and to reduce permeability -- two factors associated with improved resistance to many chemicals. Compared to portland cement concrete, higher dosage silica fume concrete has shown significantly improved resistance to the action of many solutions, including ammonium nitrate, sulfuric acid, hydrochloric acid, acetic acid, lactic acid, and hydrofluoric acid (30,31,32). Also, chemically-resistant silica fume concrete floors exposed to a variety of solutions appear to be performing as intended. The use of silica fume concrete does not completely stop chemical attack, but the frequency of repairs may be reduced significantly. With chemical-resistant applications, it is important to conduct tests to identify the appropriate materials and silica fume dosage that will improve resistance for the anticipated exposure conditions.

Silica fume concretes and mortars have consistently shown improved resistance to sodium sulfate attack -- in some cases achieving resistance equal to that of concrete made with Type V cement (1,33). Some evidence suggests that further study of the resistance to magnesium sulfate is needed (34).

Silica fume has been added to concrete, in dosages between 5 to 15 percent to prevent or delay alkali-silica reaction deterioration when high-alkali cements and reactive aggregates are present (35,36).

Indeed, nearly all cement used in Iceland has been blended with 7.5 percent silica fume to effectively prevent alkali-silica reaction problems (6).

Temperature Rise. One purpose for using silica fume is to develop mixtures with reduced heat of hydration. Here, silica fume usually replaces some of the cement. Bridges in Norway, Sweden (10), and Maine (8) have used silica fume to reduce the peak internal temperature of concrete, and at least one major dam also used silica fume concrete for this purpose (10).

Abrasion Resistance. Silica fume concrete generally shows good resistance to abrasion, which can be attributed to high strength. For this reason it has been used for pavements traveled by vehicles with steel-studded tires (10), and for a tank test track in Florida. Bridge overlays made with silica fume concrete have proved to be resistant to abrasion (8,15), and runway repairs have used specialty abrasion-resistant silica fume concretes (15).

Other Properties of Silica Fume Concrete. The relationship between static modulus of elasticity and compressive strength for silica fume concrete is roughly the same as that observed for portland cement concretes (21). As with other concretes, at very high strength levels the ACI predictor equation for elastic modulus appears to somewhat overestimate the observed results.

One creep and shrinkage study (21), which included a review of several other reports and information, concluded that the creep of silica fume concrete is similar to the creep of other portland cement concretes of equivalent strength. The drying shrinkage was found to be either about the same as or somewhat lower than the reference concretes.

ACI Committee 234 on silica fume has expressed the opinion that the fire resistance of silica fume concrete is comparable to that of portland cement concrete (37). This statement was based primarily upon ASTM E 119.

Handling

Storage. Dry bulk silica fume is stored in silos and hoppers. It may be moved via combinations of augers, pneumatic lines, air slides, and gravity. In some cases, sonic horns are used to aid in handling

the material. The densified products are handled much like cement or fly ash.

Dry silica fume is also stored in bags and crates. Big bags and crates usually contain nominally one cubic yard of material. Small bags, typically weighing 50 pounds, are used as a source of silica-fume-based products for small projects.

Slurried products are stored in tanks ranging from a few thousand gallons capacity to 400,000 gallons. In some cases, the slurried products are recirculated or otherwise agitated intermittently.

Batching. Dry bagged products (50 lbs) are usually added to mixers in whole-bag increments. The material may be added first to the mixer, and it has been added on top of the aggregates or the cement in batch hoppers. Bulk material is often dispensed from silos or hopper cars, and it is typically dispensed through the cement hopper. Slurried products are dispensed from metering devices.

Slurried products are pumped to the mixer, usually added either before or during batching of the other materials (38).

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CHAPTER 8: GROUND GRANULATED BLAST-FURNACE SLAG

General

Although there are many different types of slags resulting from production of metals from their ores, the only product suitable for use as a cementitious material is ground granulated iron blast-furnace slag. This is the glassy, granular material formed when molten iron blast-furnace slag is rapidly chilled (quenched) by immersion in water. It is this rapid quenching that retains the material in a non-crystalline (amorphous) state and makes it suitable for use as a cementitious ingredient when finely ground. The ground granulated iron blast-furnace slag will be simply referred to as slag in this report.

Specifications

When slag is separately ground for subsequent blending at the concrete mixer, ASTM Standard C 989 or AASHTO M 302 are applicable. Presently the greatest volume of slag is sold for this application. These specifications recognize three grades of slag - Grade 80, Grade 100, and Grade 120. The grade is determined by the strength relation of a 50 percent slag, 50 percent portland cement blend to the strength of C 109 mortar cubes using only portland cement (control). This relationship is referred to as the slag activity index.

When slag is blended or interground with portland cement clinker and gypsum at the cement manufacturing facility, the specification for blended cements, ASTM C 595 or AASHTO M 240, is applicable.

Quality Assurance Procedures for Slag

Complete testing of slag is time consuming, and the results often are not known until after the material has been used. Typically, the manufacturer is required to certify compliance with the specification, which in the case of ASTM and AASHTO is based on statistical format to ensure compliance with a high degree of confidence.

Since the best criterion for determining the hydraulic potential of a slag is performance, spot checks of slag activity index should be made on an

as-needed basis to compare to the results of the manufacturer. More frequent testing for fineness by Blaine or residue on the 45 μm (No. 325) sieve may be desired. In most cases manufacturers have a complete quality control program and can provide historical data on the performance of these materials if needed.

Reaction Mechanism

As shown in Table 8.1, the oxide composition of blast-furnace slag is similar to portland cement except that the proportions differ.

Table 8.1: Range of Chemical Composition of Blast-Furnace Slags in the United States and Canada

Chemical Constituents (as oxides)	Range of Composition, percent by mass
SiO ₂	32-40
Al ₂ O ₃	7-17
CaO	29-42
MgO	8-19
S	0.7-2.2
Fe ₂ O ₃	0.1-1.5
MnO	0.2-1.0

Hydration of slag in the presence of portland cement depends upon the breakdown and dissolution of the glassy structure by the hydroxyl ions released during the hydration of portland cement. Although, small immediate reactions take place when slag alone is mixed with water. The primary reaction is very slow. It is greatly enhanced in the presence of portland cement which provides additional alkali, calcium hydroxide, or sulfate to sustain the reaction (3,4).

Factors that determine the cementitious properties of slag are: a) chemical composition; b) alkali concentration of the reacting system; c) glass content of the slag; d) fineness of the slag; and e)

temperature during the early phase of the hydration process. Because of the complexity of the interrelation of all these factors, it is best to judge the suitability of any slag and cement combination by performance tests with the appropriate criteria for strength or durability.

Mixture Proportions for Concrete

Where slag is used separately in the production of concrete, trial mixtures should be made to determine if the desired properties of concrete are being achieved. The proportion of slag used is dictated by the purpose for which the concrete is to be used, the curing temperature, and the grade (activity) of the slag. Typically slag content will range between 25 percent and 75 percent of the total cementitious material.

In a blend of portland cement and slag, it is primarily the portland cement component which is responsible for the setting and early-strength properties of the concrete. Typically, the replacement of portland cement with slag will result in lower early strength up to 7 days and equal to or greater strength beyond 7 days, depending on the slag grade and curing environment. This low-early strength should be considered for form removal when early loads are expected and where cold weather is encountered.

Because of the low-early strengths, most concretes containing slag have proportions of 50 percent or less of slag. Blends greater than 50 percent slag are used only when low heat gain or high durability to sulfates and seawater is desired.

Slag is substituted on a pound for pound basis with portland cement. The specific gravity of 2.92 to 2.94 is slightly lower than portland cement (3.15) and may be considered for yield adjustment. As with pozzolans, the slag component is included as cementitious material in determining the w/c.

Slag is typically ground to a fineness greater than that of portland cement and its dense glassy structure provides improved workability. Slag concretes can accommodate up to 10 percent greater amounts of coarse aggregates in the mixture proportions. This is particularly true with low-slump paving and bridge deck mixtures when consolidation is provided by mechanical means.

Specific proportioning methods for concrete made with slag as one of the cementitious constituents

should follow the standard practices of ACI Committee 211.

Because of differences in grade and fineness, slag can react at different rates with different cements. Thus, trial batches or historical data should be reviewed to ensure that the concrete will provide the optimum properties for the job.

Effects on Unhardened Concrete

Air Entrainment

Slag does not contain carbon or other materials which may cause instability and air loss in concrete. However, when slag is used, a greater amount of AE will be needed depending on the fineness of the slag, which is typically greater than that of the portland cement replaced. The volume of cementitious material is also greater because of the differences in specific gravity. These effects are most noticeable with low slump and low w/c proportions.

Water Requirement

There is no immediate absorption of water into the slag particle because of its dense glassy structure. This results in a water demand equal to or slightly less than comparable mixtures using portland cement alone. The higher strength potential of Grade 120 slag may allow for a reduction of total cementitious material. In such cases further reductions in water demand may be possible.

Workability and Finishing

The addition of slag typically improves the workability and finishing characteristics of concrete. This is particularly true of harsh mixtures that result from fine aggregate properties and all concrete subjected to consolidation by mechanical vibration. This improvement is the result of the additional volume of fines per unit volume and the dense glassy surfaces of the slag particle. Also, research indicates that the static electric charges of the slag particles are much lower than those found in cement particles, resulting in easier dispersion of the particles through the mixture (4). As may be expected, mixtures with high total cementitious material contents can result in excessively sticky

mixtures which may be difficult to finish. The proportions of coarse aggregate should be increased to reduce the stickiness or reduce the amount of grout brought to the surface during the consolidation and finishing procedure. Because the use of slag may extend the time of setting, particularly in cool or cold weather, care should be taken not to start finishing operations too quickly. If the surface is sealed or densified prior to the cessation of bleeding, blisters may form causing subsequent loss of the material at the surface.

Bleeding

The rate and quantity of bleeding is usually less than concrete not containing slag, because of the relatively higher fineness of slag. In cold weather where retardation of the concrete may be experienced, the bleeding period will likely be increased and appropriate delays in finishing are required.

Time of Setting

The time of setting of concrete can vary considerably depending on cement brand and type, w/c, admixture use, and the placing environment. The use of slag typically retards the time of setting at high w/c and low temperatures. This effect is proportional to the proportion of slag used in cold weather. Typically, time of setting is not affected at temperatures of 80°F or higher, but can extend setting time by 2 to 4 hours at temperatures of 60°F or less. As with other concrete proportions not containing slag, the negative aspects of retardation due to cold weather can be offset by the use of accelerating admixture or protective systems. When possible, the proportions of slag should be reduced, thereby maximizing the early heat of hydration of cement to maintain an adequate environment for the finishing or other processes to proceed.

Since form pressure in designs are directly related to the setting process, consideration of form pressure is advised where retardation may be expected.

Effects on Hardened Concrete

Strength

The strength of concrete containing slag not only depends on the grade and proportions used, but also on the curing environment and the properties of the portland cement. For this reason, verification tests or previous experience should be reviewed prior to its use in job applications. Experience with Grade 120 slag support earlier findings that indicated the optimum blend for greatest ultimate strength is 40 to 50 percent replacement (5). Other data using pelletized slag of Grade 100 classification indicated that 25 percent slag yields the greatest compressive strength and 45 percent yields the greatest flexural strength (6). Although the use of slag usually results in greater ultimate strength, the early strengths at 1 to 3 days are lower than similar concrete mixtures not containing slag. Slag has a higher activation energy than portland cement, which results in an increased sensitivity to curing temperatures. At high temperatures, the slag is most reactive and at low temperatures its activity slows. Therefore, in precast products using accelerated curing, 40 to 50 percent blends will produce high 1-day strengths comparable to portland cement, and conversely at low curing temperatures (cold weather), the strengths are substantially reduced up to 14 days. In cold weather applications, the blend of slag is usually reduced to 25 to 30 percent replacement levels and in some cases where saw cutting of joints is required, the use of slag is discontinued. In hot weather applications, early strengths are increased, resulting in strength comparable to that of portland cement concrete in as little as 3 days.

As noted above, the use of slag is particularly beneficial to concrete paving applications where flexural strengths are important. The increased flexural strength is thought to be a result of the greater density of the hydration products found with the addition of slag.

Resistance to Freezing and Thawing

Tests on air-entrained concrete containing slag indicate high resistance to freezing and thawing at moderate to low w/c at blends of 50 percent or less. Blends greater than 50 percent tend to yield greater surface scaling in tests (ASTM C 666), particularly

at high w/c even though the durability factor is satisfactory (5). These results are likely caused by the immaturity of the hydration products at early ages.

Permeability

The use of slag greatly reduces the permeability of concrete depending on the amount of slag used. It is this reduction in permeability that provides high chemical resistance in aggressive environments. The permeability is reduced by a reduction in the pore size associated with the production of dense calcium silicate hydrates. As would be expected, permeability continues to decrease with age, resulting in concrete with substantially lower permeability than portland cement concrete not containing slag. It has been demonstrated that replacement of portland cement with slag has significant promise in economically reducing the chloride permeability of concrete for bridges and other structures exposed to chlorides (7).

Alkali-Silica Reactivity

The use of slag is known to be an effective alternative to the use of low-alkali cement in preventing damage due to alkali-silica reactions. The reduction in expansion caused by alkali-silica reactions is attributed to the reduction of total alkalis in the cement-slag blend, the lower permeability of the system (which demobilizes the alkali ions), and the tying up of the alkalis in the hydration process. Typically, slag blends greater than 40 percent may be used with cement alkali levels expressed as Na_2O equivalent up to 1.0 percent for the protection from alkali-silica reactions. Verification of this property may be tested by ASTM Method C 441.

Sulfate Resistance

Slag is known to increase the sulfate resistance of concrete. Generally, high sulfate resistance will be achieved with slag blends of 60 percent or greater regardless of the cement types and with blends of 50 percent when Type II cements are used. Blends of 50 percent with Type I cement will usually result in moderate sulfate resistance. ASTM Specification C 1012 may be used to determine the potential sulfate resistance with the proposed materials.

Temperature Rise

The use of slag reduces the temperature rise in mass concrete. Typically, blends greater than 60 percent are used for this application when Grade 120 slags are incorporated. With blends less than 60 percent, the rate of heat rise is decreased, but the peak temperatures may be unaffected in very large sections where the heat loss is minimal. Heat generation can be related to strength gain in that both increase with increased hydration. Therefore, the designer should make concrete proportion with 56- or 90-day strength requirements when mass concrete is applicable. Grade 100 or Grade 80 slags generally produce lower heat rise and temperatures than the more active Grade 120.

Handling, Storage, and Batching

Separately ground blast-furnace slag should be stored in separate watertight silos such as those used for cement. If common walled silos are used, the common wall must extend to the top of the silo. In some cases, contamination can occur if vents are left to accommodate dust collection systems. Each silo delivery pipe should be clearly marked to avoid confusion about which material is to be placed in a specific bin.

In batching, it is recommended that portland cement be weighed first and then followed by the slag. Slag is like cement in that normal valves are adequate to stop the flow of material. Lockout devices should be considered to ensure proper proportions of material.

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