Admixtures

- A material other than water, aggregates, cements, used as an ingredient of concrete or mortar added to the batch immediately before or during mixing.

Classification

- Chemical admixtures
- Water-reducing, retarding, accelerating, corrosion inhibitor, anti-freezing, etc
- Mineral admixtures
- Usually added to the concrete in large amounts
- Fly ash, Blast furnace slag powder, Silica Fume
- Strength index
- For the purpose of presenting a detailed description of their composition, mechanism of action, and specifications, they may be grouped into the following 3 categories: (1) surface active chemicals, (2) set-controlling chemicals, (3) mineral admixtures .

Surface active chemicals

- Mechanism of action
- Air-entraining surfactants
- The chemical formula consists of a non-polar hydrocarbon chain (water-repelling) with an anionic polar (water-attractive) (Fig.8a). Salt of wood resins.
- And the mechanism of action is illustrated in Fig.8b.

Water-reducing surfactants

- Fig.8-2a Three typical plasticizing surfactants
- The anionic polar group is joined to a hydrocarbon chain which itself is polar or hyrdophilic (water-attracting)
- Several OH groups are present in a chain.

- Water-phobic: water-dislike

Water-reducing surfactants

- ***When a small quantity of water is added to the cement*, *without the presence of surfactant***, a well dispersed system is not attained because, first, the water possesses high surface tension (hydrogen-bonded molecular structure: water surface area minimum), and second, ***the cement particles tend to cluster together or form flocks*** (attractive forces exists between positively and negatively charged edges, corners, and surfaces when crystalline minerals or compounds are finely ground). Fig.8-2c
-

Cont.

- With this kind of surfactant, the cement particles are hydrophilic (water-attractive). **As a result of layers of water dipoles surrounding the hydrophilic cement particles, their fluctuation prevented and a well-dispersed system is obtained.**

Applications

- Air-entraining admixtures
- Resist freezing and thawing action
- Improve workability
- (make cement particles water-repelling)
- Water-reducing admixtures ***(Table 8-1 will be explained)***
- Increase workability (consistency)
- Higher compressive strength
- Cement saving
- The period of effectiveness of surfactants is rather limited
- ***Because the formation of ettringite engulf the surfactants.***

Superplasticizers (high range water reducing admixtures) 20%-25%

- ***They consist of long-chain, high-molecular-weight (20,000-30,000) anionic surfactants*** with a large number of polar groups in the hydrocarbon chain.
- ***When adsorbed on cement particles, the surfactant imparts a strong negative charge***, and helps to lower the surface tension of the surrounding water considerably and greatly enhances the fluidity of the system.
- Up to 1% by weight of cement
- Segregation is generally not encountered

- Water reduction in the range of 20-25% without reducing the consistency.
- Due to a greater rate of hydration in the well dispersion system **(Fig.8-3)**, concretes containing super-plasticizers shows higher strength than reference concretes having the same W/C.
- High-early strength can be obtained – advantageous to concrete-product industry.
- Explanation about Table8-2.
- High water range reducing AE admixture
- **高性能AE減水剤　ポリカルボン酸系（立体障害）**
- **Poly-carboxylic acid**

Set controlling chemicals

- Chemicals that can retard or accelerate the setting time and rate of strength development.
- Forsen divided retarders and accelerators into several groups. A modified version is shown in Fig.8-4.

Mechanism

- A hydrating portland cement paste as being composed of certain anions (silicate ,aluminates and sulphates) and cations (calcium , sodium).
- Most chemical admixtures will ionize in water.
- Due to their limited solubility,
- Thus they influence the dissolution of the cement compounds.

- 1. ***An accelerating admixture*** must promote the dissolution of ***the cations*** (Ca^{2+}) and ***anions*** (***silicate ions***) from the cement, ***especially silicate ions***.
- 2. ***A retarding admixture*** must impede the dissolution of the cations and anions, especially ***aluminate ions***. AlO_2^-
- It is possible for the same salt to change its role and become an accelerator instead of a retarder.
- It should be noted that $CaCl_2$, 1 to 3 % by weight of cement, **was** most commonly used accelerator for plain concrete. (Fig.8-5 (a))

- 3.the presence of cations (K^+, Na^+) reduces the solubility of Ca^{2+}, but tends to promote the solubility of silicates
- 4. the presence of certain anions (Cl^-, NO_3^- or SO_4^{2-}) reduces the solubility of silicates but tends to promote the solubility of Ca^{2+}.
- In small concentration the former effect is dominant, but in large concentration latter effect becomes dominant.
- The setting time is gradually increased when the amount of gypsum ($CaSO_4 \cdot 2H_2O$) added. Because of low solubility.

- Applications
- Accelerating admixtures : useful in cold weather
- Retarding admixtures :
- Compensation for adverse ambient temperature conditions particularly in hot weather
- Control of setting of large structural units to keep concrete workable throughout the entire placing period.
- For the elimination of cold joints and discontinuities in large structural units.

Mineral Admixtures

- Pozzolanic、cementitious, both pozzolanic and cementitious
- In Table8-6, summarization is shown. ***Cementitious and pozzolanic, highly active pozzolans, normal pozzolans, weak pozzolans***
- Low-calcium FA, granulated iron blast-furnace slag, high-calcium FA
- Natural materials , and By-product materials

Natural materials

- The ***quick cooling*** of the magma, composed mainly alumino-silicates, results in the formation of glass phases of disordered structure.
- Volcanic glasses
- Santorini earth of Greece, Bacoli Pozzolan of Italy, Shirasu pozzolan of Japan (***now, Prof.Takewaka, Kagoshiman Univ. is serous.***)
- Volcanic tuffs（凝灰岩類）
- Calcined clays or shales, Diatomaceous earth（ケイソウ土）

By-product materials

- Ashes from combustion of coal and some crop residues, volatilized silica from certain metallurgical operations, and granulated slag from both ferrous and non-ferrous metal industries are the major industrial by-products that are suitable for use as mineral admixtures in portland cement industry.
- BFS,FA,SF , rice husk ash, bagasse ash etc.

Fly ash

- During combustion of powdered coal in modern power plants, most mineral impurities such as clays, quartz, and feldspar will melt at the high temperature.
- The fused matter is quickly transported to lower temperature zones, where it solidifies as spherical particles of glass.
- Some of the mineral matter agglomerates forming bottom ash, but most of it flies out with the flue gas stream and called fly ash. This ash is substantially removed from the gas by electro-static precipitators .

Two categories:

- Containing less than 10% CaO Class F (mostly in Japan)
- Containing more than 10% CaO, Class C (Mae Moh)
- ClassF
- The low-calcium fly ashes, due to the high proportions of silica and aluminum, consist principally of aluminosilicate glasses.

- ClassC
- The high-calcium fly ashes are in general more reactive because they contain most of the Ca in the form of reactive crystalline compounds (C3A,or CaOSO3,etc)., also contain enough Ca ions to enhance the reactivity of the aluminosilicate glasses.
- High carbon content is no good.（why?何故でしょう？）
- Solid spheres of glasses, cenospheres(completely empty), plerospheres (packed with small spheres)
- Particle size is from <1 μm-100 μm, with more than 50% under 20 μm .

- Low-calcium fly ash, which usually does not contribute to the strength of portland cement concrete until after about 4 weeks of hydration.
- High-calcium fly ash or BFS may become apparent as early as 7 days (strength).
- Also in higher temperature, they can perform much better.(advantages in hot countries.)

Blast-furnace slag

- In the production of cast-iron, the liquid slag is rapidly quenched from a high temperature by either water or a combination of air and water, most of the lime, magnesia, silica, and alumina are held in non-crystalline or glassy state..
- The water quenched product is called granulated slag due to the sand-size particles, while the slag quenched by air and a limited amount of water which is in the form of pellet is called palletized slag.
- Both products develop satisfactory cementitious properties.

- The glass chilled from a higher temperature and at a faster rate, will be more reactive.
- Slag particles less than 10 μm: contribute early strength up to 28 days
- 10 to 45 μm : contribute to later strength under 45 μm:5000cm2/g
- larger than 45 μm: difficult to hydrate .

Condensed silica fume (Silica Fume)

- By-product of induction arc furnaces in the silicon metal and ferrosilicon alloy industries.
- Reduction of quart to silica at temperature up to 2000°C produces SiO_2 vapors, which oxidize and condense in the low temperature zone to tiny spherical particles consisting of noncrystalline silica.
- The order of 0.1 μm (2 orders of magnitude difference) 20-25m2/g 200,000cm2/g
- Highly pozzolanic
- Difficult to handle so necessary to use water-reducing admixture
- Over 90% noncrystalline silica (JSCE standard)

Rice husk ash

- Rice husks are the shells produced during the dehusking operation of paddy(もみ)rice.
- Each ton of paddy rice produces about 200kg of husks, which on combustion yield 40kg of ash.
- Industrially produced samples of this material showed 50 to 60 m2/g (500,000-600,000cm2/g) surface area by nitrogen adsorption.）.
- To keep the burning temperature just below 700 is very difficult. Is there anyone who knows?

Applications

- Improvement in workability
- When fresh concrete mixtures that show a tendency to bleed or segregate, it is well known that incorporation of finely divided particles generally improves workability by reducing the size and volume of voids.
- Fly ash (spherical particles and glassy texture) make it possible to reduce the amount of water required for a given consistency. BFS may make.
- The use of very high surface materials , silica fume and rice husk ash, tends to increase the water requirement .

Durability to thermal cracking

- The use of mineral admixture offers the possibility of reducing the temperature rise almost in a direct proportion to the amount of portland cement replaced by the mixture.
- Because under normal conditions, these admixtures do not react to a significant degree for several days.
- Portland cement replacement by fly ash has been practiced in the USA as well as in Japan.
- Whereas high temperature exposures can be harmful to portland cement concrete, concrete containing mineral admixtures may benefit from thermal activation.

Durability to chemical attacks

- Since the pozzolanic reaction involving mineral admixtures is capable of pore refinement, which reduces the permeability of concrete, both field and lab studies have shown considerable improvement in the chemical durability. 10times or less
- 40-65% BFS, 30-40% low-calcium FA, 10%SF have been found to be quite effective in limiting AAR.
- Mineral admixtures improves the resistance to acid water, sulfate water and sea water.
- Reduction in permeability as well as a reduction in the calcium hydrate content.
- If and only if there is sufficient curing.(very difficult in practice:これが大問題）

Production of high-strength concrete

- Industrial applications of 70-80Mpa compressive strength concrete containing SF and water-reducing admixtures are reported (Japan: first by Takenaka Co.)

Concluding remarks

- Most of the problems lie in the incompatibility between a particular admixtures and a cement composition and etc..（there are many impurities. どちらにもいろいろな不純物）
- It is highly recommended to carry out laboratory tests involving field materials and conditions before actual use of admixtures in concrete construction.