(52)

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Mineral Admixtures in Concrete: State of the Art and Trends

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Synopsis : With increasing acknowledgement of the importance of mineral admixtures, many kinds of by-product mineral admixtures have become wide spread as a very important constituent of cement concrete. By-product mineral admixtures such as fly ash, silica fume, rice husk ash and ground granulated blast-furnace slag are attracting much attention as materials not only contributing to the improvement of concrete performance, for example, high strength, high durability and reduction of heat of hydration, but also are indispensable for the reduction of energy and carbon dioxide generated in the production of cement. This paper describes the current status of by-product mineral admixtures for concrete and future outlook for them.

Keywords: Blast furnace slag; durability; fly ash; fresh concretes; hardened concretes; heat of hydration; mineral admixtures; rice husk ash; silica fume; strength.

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INTRODUCTION

The history of cement and concrete is generally assumed to have begun in ancient Egypt and Greece, although recent reports claim that it dates back as far as 9000 years ago (1). Natural pozzolans were used in ancient cement and concrete products, however it is relatively recently that the use of by-product mineral admixtures, such as fly ash and ground granulated blast-furnace slag has become widespread. Today, mineral admixtures are attracting much attention as materials contributing to the improvement of concrete characteristics as well as to the reduction of the energy and carbon dioxide generated in the production of cement. In particular, they are indispensable for the improvement of concrete performance contributing, for example, to high strength, high durability, and reduction of heat of hydration.

This paper outlines the current status of by-product mineral admixtures for concrete and the future outlook for them. With increasing acknowledgement of the importance of mineral admixtures, there is already considerable published literature on the subject. The contents of the published reports vary depending on the author's area of specialization. There are many excellent papers including those by Mehta(2) and Malhotra(3), and I feel some hesitation about presenting yet another review paper on mineral admixtures. However, considering the fact that not many of the published reports include data or describe conditions in Japan, I have decided to delve into this subject. For this reason, this paper contains several references and data of Japanese origin.

CLASSIFICATION OF ADMIXTURES

The term,admixture, includes both mineral and chemical additives that are added to concrete. In general, the use of chemical additives is limited to less than 5% by weight of cement, whereas mineral admixtures are used in much larger proportions.

In Japan, according to the standard specifications for concrete(4), mineral admixtures are classified according to the areas of application:

(a) Those from which pozzolanic activity can be expected, such as fly ash, silica fume, volcanic ash, siliceous white clay and diatomite. react with the presence of cement.

(b) Those from which hydraulicity can be expected, such as ground granulated blast-furnace slag. → react independently

(c) Those which cause expansion in the hardening process, i.e. expansive additives.

(d) Those which contribute in gaining high strength as a result of autoclave curing, such as siliceous powders.

(e) Those used for coloring such as pigments.

(f) Miscellaneous such as admixtures for high strength, polymers,and fillers.

The scope of this paper is limited to the first two classes. Accordingly,the mineral admixtures discussed in this paper are fly ash, silica fume, rice husk ash, and granulated blast-furnace slag. In addition to their characteristics,their effect on properties of fresh and hardened concrete as well as durability of concrete will be discussed.

FLY ASH

Fly ash is the general term for fine coal ashes that are produced by the burning of coal in power plants or industrial boilers. Generally, 15~20% of burnt coal takes the form of ash. Although the percentage varies slightly depending on the kind of coal, 70~85% of the ash produced as a result of burning of coal is fly ash. Initially, the fine powders were emitted from flues into the air, however in the interest of preventing air pollution, technology allowing for the scavenging of the fine powders in the flues was developed. Fly ash was first put into practical application in the form of a concrete admixture at "Hungry Horse Dam" built by the U.S. Bureau of Reclamation. Thereafter, fly ash was widely utilized as mineral admixture for concrete in massive hydroelectric structures in the United States.

Table 1 lists the amount of mineral admixtures produced as by-products in various countries around the world and the amount available for use, based on a report from RILEM TC-73. The table indicates that fly ash is more widely used than other admixtures. At the four ACI/CANMET conferences on mineral admixtures organized by Malhotra, many reports on fly ash are presented. This reflects the fact that fly ash is the subject of considerable research in the world.

The total amount of fly ash produced as a by-product in 1989 was on the order of 400 million tonnes annually; 90 million tonnes were produced in the former Soviet Union, 55 million tonnes in China, 48 million tonnes in the United States, and 36 million tonnes in India, followed by Poland, Germany, Turkey and the UK. In Japan, the amount of fly ash produced is relatively small; however, since space for disposal cannot be secured due to the small land area, effective utilization of fly ash is an important issue.

The standards for fly ash were stipulated in 1954 by the American Society for Testing and Material. Today, fly ash is broadly classified into the following two classes.

Class F:	Fly ash normally produced by burning anthracite or bituminous coal, and usually has less than 5% calcium oxide. Class F fly ash has pozzolanic properties only.
Class C:	Fly ash normally produced by burning lignite or sub-bituminous coal. Some class C fly ash may have lime content in excess of 10%. In addition to pozzolanic properties, Class C fly ash also possesses cementitious properties.

Characteristics of fly ash

Most of the fly ash that is used by concrete industry is Class F; Class C is mostly produced only in the United States and Canada(6).
In general, the chemical constituents comprising Class F fly ash include SiO_2 (50~60%), and Al_2O_3 (20~30%), as well as Fe_2O_3, CaO, and carbon.

Although fly ash with less than 5% CaO does not have hydraulicity in itself, it solidifies when mixed with water due to the pozzolanic reaction, in which alkali generated as a result of the hydration of portland cement, react with SiO_2 and Al_2O_3 contained in fly ash. Since fly ash is produced by rapid cooling and solidification of molten ash, a large portion of components comprising fly ash particles contain amorphous products. The amorphous characteristics greatly contribute to the pozzolanic reaction between cement and fly ash.

The specific gravity of fly ash varies in the range 2.1~2.6. The specific surface area is affected by the kind of coal, the type of boiler, and burning conditions. It is difficult to control these conditions since fly ash is only a by-product, The quality of fly ash may fluctuates during the course of a day which is undesirable from the viewpoint of users. Most of the ignition loss consists of unburnt carbon which can adsorb chemical admixtures, such as air entraining agents. Therefore, if the content of unburnt carbon is large, the amount of chemical admixture necessary to obtain the required amount of air tends to increase.

One of the important characteristics of fly ash is the spherical form of the particles. This contributes to improvement in the concrete flowability when fly ash is used as a concrete admixture. However, a combination of factors such as the coal type, the burning temperature, the kind of boiler, and operation condition may lead to the formation of coal ash that is not suitable for use as pozzolan, i.e., containing nonspherical particles or with large ignition loss. The test for fully compacted dry density is proposed to indicate these characteristics(7). Using this test, the appropriateness of a fly ash for use in concrete can be determined. For concrete mixtures with water-binder ratios of 45 and 55%, Fig. 1 shows the water-content ratio (which is defined as the ratio of water content between the concretes with fly ash and without fly ash) in relation to the compacted bulk density of fly ash.

Performance of concrete containing fly ash

if more unburnt c more will be the loss

Fresh concrete

As described in the above sections, when fly ash is mostly composed of spherical particles and has small ignition loss, the unit water content necessary to produce concrete with desired slump can be reduced by replacing part of the cement with fly ash (Fig. 2). In such a case, with the reduction of the unit water content, bleeding and drying shrinkage can also be reduced(9). Moreover, since fly ash itself is not highly reactive, the heat of hydration can be reduced through replacement of part of the cement with fly ash. Owing to this characteristic of fly ash, concrete containing fly ash is very suitable for use in mass structures and proves advantageous when used in dams and abutments of large bridges. Fig. 3 shows the characteristics of heat of hydration of concrete containing fly ash(10).

It should be noted, however, that fly ash produced under certain conditions of coal type and boiler temperature may be of the amorphous form, but the content of spherical particles may be small, and unburnt carbon is usually present as large lumps. When such a fly ash replaces a part of the cement, the unit water content increases and this type of fly ash does not prove to be beneficial (Fig. 4).

Hardened concrete

Fly ash, when mixed with concrete, contributes to the strengthening of concrete due to its pozzolanic reactivity; however, since the pozzolanic reaction proceeds slowly, the initial strength of fly-ash concrete tends to be lower than that of concrete without fly ash. Fly-ash concrete, however, offers greater strength at later age, which may exceed that of the concrete without the fly ash. The pozzolanic reaction also contributes to making the texture of concrete dense, resulting in the decrease in water permeability and gas permeability. Since the pozzolanic reaction proceeds under the presence of water, enough water should be available during curing. In this sense, the application of fly ash to concrete structures immersed underwater, such as dams, proves beneficial in terms of the improved long-term strength and water-tightness. dam, marine structure, port & harbour

Durability

After sufficient moist curing, the texture of concrete containing fly ash become dense due to the pozzolanic reaction. Such concrete offers high resistivity against degradation due to the infiltration of deleterious substances.

denseness
carbonation
AAR

Replacement of part of the cement with fly ash can be a disadvantage in terms of neutralization of the alkali content due to pozzolanic reaction. However, according to the published data, concrete with fly ash shows similar depth of carbonation to concrete without fly ash, as long as the compressive strength level is same (Fig.5). Likewise, the same level of resistance against frost damage can be obtained, irrespective of the inclusion of fly ash, as long as similer levels of strength and air content are maintained.

The corrosion resistance in sea water is improved over that of ordinary concrete due to dense texture; resistance against infiltration of harmful ions is improved, and C_3A and free $Ca(OH)_2$ content are reduced. It is also recognized that the addition of fly ash contributes to reduction of the expansion due to alkali-aggregate reaction. There are many theories which explain the mechanism, which is yet to be verified. The dilution effect of alkali and reduction of the water permeability due to the dense texture are some of the factors that are considered responsible for this phenomenon. In conclution, although it is an industrial waste, fly ash of good quality when used as concrete admixture will improve the quality of concrete. In particular, the long-term strength and durability are significantly improved and heat of hydration is reduced. Thus, fly ash is a mineral admixture that is indispensable for the preparation of high-performance concrete.

SILICA FUME

0.1μm

Silica fume is an industrial by-product consisting of ultrafine particles. It is recoverd from electric furnaces by means of dust collectors from the waste gas emitted during the production of ferro-silicon alloys or silicon metal. According to the RILEM TC 73 classification, silica fume is a highly active pozzolan. However, it is not available in as large amounts as fly ash, and is also more expensive.

Initially, silica fume used to be released into the atmosphere from gas flues as was the case with fly ash. In the 1950's, however, due to environmental concerns, the removal of silica fume from flue gases was required, and therefore the utilization of silica fume as a concrete admixture was studied. The earliest studies were conducted in Northern European countries, including Norway, one of the main countries producing silica fume. In 1952, concrete with 15% of cement content substituted by silica fume was used for the first time in the construction of a tunnel in Oslo, Norway. At the beginning stage of the practical use of silica fume, it was used simply for the purpose of reducing the amount of cement. However, since silica fume consist of ultrafine particles, addition of silica fume tends to increase the water content. In the 1960's, superplasiticizers (high range water-reducing agent), which are able to cause considerable reduction of water content, came into practical use, and it was shown that very strong and highly durable concrete could be obtained when silica fume was used together with a superplasticizer. Since 1970's, considerable research on this subject has been conducted in countries such as Canada, United States, Germany, and France.

In the case of silicon metal and ferro-silicon alloy, 550kg and 350kg of silica fume, are produced respectively per 1 tonne of target product. The higher the productivity of silicon alloy is, the smaller the amount of silica fume . The amount of silica fume produced per 1 tonne of silicon metal is thus expected to decrease further in the future. At present, major countries producing silica fume include Norway, Canada and the United States, where abundant and inexpensive electric power is available. Production of silica fume would be possible in China and Eastern European countries if scavenging equipment were installed. Presently, estimated annual production of silica fume in the world is of the order of 1.6 million tonnes.

Characteristics of silica fume

Silica fume come in three forms: powder, condensed and slurry. In slurry, chemical admixtures are premixed. To produce condensed silica fume, high pressure is applied to silica fume powder. Table 2 shows the chemical composition and physical properties of silica fume(13). Silica fume generally contain more than 90% SiO_2. However, the content of SiO_2 and the degree of amorphousness may differ considerably, depending on the method of production. In general, the color of silica fume is gray, but it can range from whitish to blackish depending on the content of carbon. The true specific gravity is 2.1~2.2, and the bulk weight is 250~300kg/m^3. The bulk density is significantly small as compared to portland cement. Silica fume powder consists of spherical, fine particles with specific surface area approximately 20,000m^2/kg, which is 50~60 times finer that of portland cement and is finer than the particles in cigarette smoke.

Performance of concrete containing silica fume

Fresh concrete

Since silica fume is ultrafine powder, when it is mixed with concrete the viscosity of the concrete increases and flowability decreases, resulting in reduced concrete slump. Thus, the water content necessary to obtain the desired slump increases(14). This can be prevented through use of a superplasiticizer. In other words, the use of silica fume as admixture is not possible without superplasticizer.

Plastic shrinkage
initial state
→ more heat

With regard to the air entrainment, due to the presence of carbon and ultrafine nature of silica fume powder, air entrainment tends to be difficult, and therefore, with the increase of silica fume content (SF/(C+SF)), the amount of air entraining agent needs to be increased(Fig. 6). Also, with the increase of silica fume content, the segregation tendency in fresh concrete becomes less. When the silica fume content is 10% or higher, neither material segregation nor bleeding occurs even when the slump is 15~20cm(16). It is reported that concrete containing silica fume is vulnerable to plastic shrinkage cracking, therefore, sheet or mat curing should be considered. As shown in Fig. 7, addition of silica fume promotes heat generation at the initial stage of hydration(17). It is reported however that the total amount of heat generated by silica-fume concrete is less than that of ordinary concrete for two days .

Hardened concrete

Mortar and concrete containing silica fume show outstanding characteristics in the development of strength. Fig. 8 shows an example; compressive strength of 60~80Mpa can be obtained relatively easily, although these values may differ depending on the kinds of silica fume and cement, content of silica fume, and curing method and age(18). This property is explained as resulting from the decrease in the volume of large pores in concrete, hence making the concrete texture dense. When accelerated curing such as steam curing and autoclave curing are utilized(Fig. 9), the use of silica fume is also effective in facilitating the development of strength at early age, since the pore size distribution and pore volume significantly differ from those of concrete subjected to standard curing. In such a case, it is verified that compressive strength of 150MPa can be obtained(19). As is shown in Fig. 10, the Young's modulus of elasticity of silica-fume concrete is smaller than that of concrete without silica fume, at the same level of compressive strength. This is because the content of cement paste, which has a lower Young's modulus of elasticity than aggregate increases due to the addition of silica fume.

Durability

As a result of a thorough review of previously published reports, the durability aspect of the concrete containing silica fume are shown in Table 3. The table denotes the number of reports reviewed dealing with the contribution of silica fume to improvement of resistance to frost damage, carbonation, etc., and whether or not the use of silica fume was effective. According to Table 3, effects of silica fume include improved resistance to infiltration of chloride, and increase in electric resistance, watertightness and airtightness. Contradictory data are reported on ~~the effect of silica fume~~ on resistance to frost damage and suppression of alkali-aggregate reaction, as discussed below.

frost damage
AAR
⇑
??

Many studies have been carried out on the resistance of concrete containing silica fume to frost damage, and some of the conclusions contradict each other. Approximately 60% of these reports conclude that the silica-fume concrete offers higher resistance to frost damage than concrete without silica fume, 10~20% (*) conclude that both offer the same level of resistance, and 20~30% conclude that the resistance offered by silica-fume concrete is lower. From Japan and the Scandinavian countries, there are many reports concluding that silica fume contribute to improving the resistance to frost damage, while many reports from Canada conclude the opposite. This discrepancy is attributable to the fact that the evaluation procedure can differ depending on the target of observation, such as, between the case where scaling degradation on the surface is mainly observed and the case where cracks developing on the surface and inside the concrete are mainly observed. Other factors responsible for the discrepancy include differences in the kinds of silica fume, silica fume content, air content and concrete mix proportions. At present, an appropriate amount of entrained air must be supplied irrespective of the concrete mix proportion, conforming to recommendations by the ACI Committee 226 (21) and Canadian Standards Association(22).

With regard to whether or not silica fume is effective for the suppression of alkali-aggregate reaction, some researchers report that it is effective, others conclude that while it is effective, addition of silica fume in small quantities actually increases the expansion. Some researchers indicate that effects vary depending on the kind of silica fume and the type of reactive aggregate. In conclusion, the use of fly ash and blast-furnace slag seems to be more appropriate for this purpose ~~especially because silica fume also happens to~~ be relatively more expensive.

RICE HUSK ASH

Rice husk ash (called rice hull ash in the United States), as indicated by its name, (*) is obtained by burning rice husks. Although ashes can be obtained by burning various kinds of grain husks and straws, rice husk ash has the largest SiO_2 content, and when properly burnt, it can be highly utilized as a concrete (*) admixture. Like silica fume, rice husk ash exhibits highly pozzolanic characteristic and contributes to high strength and high impermeability of concrete(7).

Earlier, rice husks used to be burnt in rice paddy farms. However, open-field burning of rice husks causes air pollution, and it is now required that they be burnt at well-managed facilities.

Characteristics of rice husk ash

In the beginning, since temperature control was not adequate, ashes produced contained a large amount of residual carbon, and the amorphous silica content was low. Ashes of this type were effective as concrete admixtures utilized only if steam curing was employed at factories(23). However, in 1972, Mehta(24) reported that the amorphous content of silica in rice husk is considerably affected not only by burning temperature but also by cooling conditions. Subsequent studies conducted at the University of California revealed that amorphous rice husk ash exhibited excellent pozzolanic characteristics even when used in products without steam curing.

As described above, physical properties of rice husk ash are greatly affected by burning conditions. When the combustion is incomplete, a large amount of unburnt carbon is contained in the ash and it presents a blackish color. However, when combustion is complete, gray to whitish ash is obtained, although the gradation depends on the kind and maturity of rice husk as well as on the method of burning. It is also verified that the amorphous content depends on burning temperature and holding time. According to the report from the University of California, optimum properties can be attained when rice husks are burnt at 500~700°C and held for a long time, or when they are burnt at a higher temperature of 700~800°C and held for a short time. In case, however, they are burnt at a temperature higher than 800°C, specific surface area drastically decreases due to the sintering effect as shown in Table 4.

The chemical composition of the rice husk ash produced by utilizing the fluidized bed type furnace is reported to be: SiO_2 80~95%, K_2O 1~2% and unburnt carbon 3~18%. However, the high-carbon rice husk ash samples were found to exhibit pozzolanic characteristics identical to those of the low-carbon rice husk ash samples(26).

Performance of concrete containing rice husk ash

The pozzolanic activity of rice husk ash is not only effective in strengthening the
a concrete, but also in increasing the resistance to chloride penetration, as shown in
furnaTable 5. However, Mehta pointed out in his recent report(26) that not only at
obtaine water-cement ratio, but also at high water-cement ratio, the use of rice husk
very effective to improve impermeability. With 15% rice husk ash addition
The specific ht of cement), the chloride permeability with the 0.7 W/C concrete was
that of cement, b

reduced from 9910 to 1630 coulombs, and with the 0.5 W/C concrete it was reduced from 6860 to 1100 coulombs. Thus, the use of rice husk ash as an admixture for commonly used concrete appears to provide simple and economic approach for making durable concrete structures in the future.

Beside use as admixture, various applications of rice husk ash in concrete have been studied. Applications to roofing(27) and roller compacted concrete(28) have already been reported. However, further studies must be awaited before practical application in industrial products is realized. .

GROUND GRANULATED BLAST-FURNACE SLAG

Blast furnace slag is a by-product of pig iron manufacture. When quenched rapidly with water or air to a glassy state and finely ground, it develops the property of latent hydraulicity. Conventionally, rapidly cooled blast furnance slag is ground simultaneously with cement clinker, or separately ground and then mixed with cement, and marketed as "Blast-furnace slag cement". Since it has hydraulic characteristics, ground granulated blast-furnace slag can also be used as a mineral admixture in conerete.

Ground granulated blast-furnace slag has chemical components similar to that of Portland cement. Due to hydraulicity, therefore, its use contributes not only to improvement in concrete performance, but also to resource and energy savings. The first ground granulated blast-furnace slag, as an industrial product, was produced in Germany in 1923, and was called Thurament.

Characteristics of ground granulated blast-furnace slag

The chemical composition of ground granulated blast-furnace slag is the same as that of blast-furnace slag since it is produced by pulverizing blast-furnace slag. However, in some cases, different values are obtained when a small amount of gypsum has been added.

Table 6 shows the physical-chemical requirements for ground granulated blast-furnace slag in various countries(29). Major chemical constituents are SiO_2: 30~35%, Al_2O_3: 12~15%, CaO: 40~43%, and MgO: 5~10%; minor constituents are Fe_2O_3, MnO, SO_3, TiO_2 and Na_2O. The Japanese Standard Specification contains basicity $(CaO+MgO+Al_2O_3)/SiO_2$, as an index of the activity of blast-furnace slag. Generally higher values than the minimum specified value (1.4) are obtained, indicating the high activity of Japanese blast-furnace slag.

The specific gravity of slag is approximately 2.9, which is slightly lower than that of cement, but higher than that of fly ash; hence, material segregation is less likely to occur in slag-cement blends.

Typically, the fineness of blast-furnace slag is 3000~4000cm^2/g (Blaine). Since finer the slag powder, the greater the hydraulic activity, ultrafine powders with fineness of 6000 to 8000cm^2/g, or even higher are being used in many countries(30).

Performance of concrete containing ground granulated blast-furnace slag

Fresh concrete

When a part of cement is replaced with ground granulated blast-furnace slag, the characteristics of the concrete are naturally affected by the fineness of the ground granulated blast-furnace slag, and its replacement ratio.

Fig. 11 and 12 show the results of the experiment examining the effects of the use of ground granulated blast-furnace slag on the workability of concrete. The unit water content necessary to obtain the same slump decreases with the increase in the slag content(31), and also the fineness of slag(32). This is because the surface configuration and particle shape of slag powder are different than those of cement. In addition, water used for mixing is not easily adsorbed by slag particles since the reaction rate of slag is slower than that of cement.

The bleeding-suppression effect is negligible with slag powder of 4000cm^2/g fineness. However, a significant beneficial effect is observed with slag powders of 6000 and 8000cm^2/g fineness.

Hardened concrete

It has been shown that slag substitution for cement is responsible for the delay in the development of initial strength, and the effect is especially large when the concrete mixture is maintained at a lower temperature.
Heat of hydration of concrete containing slag powder decreases with the increase in the slag powder content. However, when curing is performed at higher temperatures (30^{0}C or higher), there may not be any reduction in the heat of hydration; in fact, the heat of hydration may be greater in the case where slag powder is not added (Fig. 13) when the slag powder content is 50% or less. The heat of hydration is also affected by the fineness of slag powder, gypsum content, basicity, and amorphousness of slag. Generally, when these values are low, the heat of hydration decreases. However, it has been proven that the effects of slag powder and curing temperature are much greater. As shown in Fig. 14, the rate of adiabatic temperature rise of concrete containing slag powder decreases when the slag content is 70% or less, but the ultimate value of adiabatic temperature rise is equivalent to or higher than the case when no slag is added(33). However, when the slag content is 90%, the value tends to decrease

by a large amount.

Durability

Concrete containing slag as a mineral admixtures generally offers better chemical resistance due to improved watertightness, since the concrete texture becomes dense. Slag is also useful for the prevention of corrosion of reinforcement, since it suppresses the infiltration of chlorine ions. The alkali-aggregate reaction can be suppressed by the use of concrete with higher slag powder content as shown in Fig. 15.

Table 7 shows the effects of different combinations of fineness and slag powder content on properties of concrete.

CURRENT STATUS OF MINERAL ADMITURES IN JAPAN AND FUTURE OUTLOOK

In the previous sections, mineral admixtures for concrete currently in wide use are described. In this section, usage of some noteworthy applications in Japan and the future outlook for mineral admixtures will be presented.

First, the author would like to discuss, the ultralow-heat-type cement, which is being utilized in the concrete used for anchorages and piers of Akashi Kaikyo Bridge (3-span suspension bridge,total length 3,900m, central span 1,990m). The Honshu Shikoku Bridge Authority has overseen the construction of many large-scale bridges besides the Akashi Kaikyo Bridge. In the construction of these bridges, they took measures such as the use of low-heat cement, precooling, and post-cooling to avoid the development of thermal cracking in mass concrete. In most cases, however, thermal cracks due to the heat of hydration of cement were observed at anchorages and piers. These thermal cracks do not pose serious problem from the view point of concrete strength since the cracks are small. However, from the viewpoint of aesthetic beauty and long-term durability, it is desirable to prevent development of these thermal cracks. This has led to the development of ultra low-heat-type cement with sufficient initial strength. The Honshu Shikoku Bridge Authority specified a standard concrete mix for construction and contracted cement manufacturers to develop cement which satisfied the requirements of concrete strength and adiabatic temperature rise (Table 8).

Cement manufacturers conducted studies aiming to develop a cement meeting the above described conditions, by blending ground granulated blast-furnace slag, fly ash and cement clinker. As a result, the two-component and three-component cements listed in Table 9 have been developed.
Presently, construction of the pier has already been completed using this type of

cement for both underwater and above-water structures. Construction of the anchorage has also been proceeding steadily and will soon be completed. Development of thermal cracks is very rare, due to the use of the ultra low-heat-type cement. However, concrete made of this type of cement may be neutralized in a short time, and may have poor durability. Therefore, precast concrete facing panels made of polymer impregnated concrete are used for the above-water pier structure, and precast concrete panels made of reinforced concrete are used for the above-water anchorage structure, so that the bulk concrete is not directly exposed to the atmosphere.
In the next step, use of clinker of Berite-based cement, in which C_2S content in cement clinker is higher than 50%, was considered to be a practical means of slowing the neutralization of concrete, and several cement manufacturers began producing Berite-based cement. Composite cement with 30% fly ash and slag powder content each, added to the Berite cement has already been put into practical application as ultralow-heat-type cement, which provides reasonable temperature rise(Fig. 16), and initial strength(Fig. 17).

Second, the author would like to describe the use of a large amount of mineral admixture with the expectation of benefiting from its effect as a fine powder rather than that as a cementing material. In the construction of reinforced concrete, when reinforcement is very closely arranged, especially when a sheath for the prestressed concrete steel strand is also present, it may be difficult to completely fill the voids with concrete. In this case, high-fluidity concrete was developed (with a slump of 25cm or larger) which can fill space by its own weight, and consolidation of concrete by means of a vibrator is not needed. When this type of high-fluidity concrete is placed, generally, material segregation and bleeding develop. Countermeasures for these problems include the increase of the fines in the concrete mixture, use of thickening agents or combination of both. In all the cases, increase of water content is prevented through the use of a superplasiticizer. Addition of a large amount of fly ash or ground granulated blast-furnace slag, for the purpose of increasing the fines, also results in improved long-term strength and lower heat of hydration. When a high long-term strength is not particularly desired, limestone powder is utilized. Limestone powder of 5000~7000 cm^2/g is available commerically, and the fineness can be selected depending on the fineness of cement(37).

Lastly, the author would like to describe a historical structure containing a natural mineral admixture. Approximately 100 years ago, the first ocean breakwater in Japan was constructed at Otaru Port, Hokkaido, Japan. Learning a lesson from the development of cracks in concrete blocks at Yokohama and Kobe Ports, Isamu Hiroi, the first Director of the Otaru Port Authority proposed the use of pozzolanic material together with cement. Volcanic ash was used as an admixture for concrete in the structure, and at the same time, 60,000 mortar briquette specimens were fabricated using different combinations of various kinds of cement, volcanic ash and curing methods, and the long-term testing of these specimens was undertaken. The fabrication of specimens was initiated in 1896, a year preceding the construction of the breakwater at Otaru Port, and continued until 1937. Under the Chairmanship of the author, a committee on Otaru Port concrete durability has recently tested the cores obtained from the 100-year old structure. The results have ensured the long-term stability of the breakwater(38). It is noteworthy that an appropriate evaluation of the use of mineral admixture was made 100 years ago, and a long-term testing program was pursued.

Judging from the conditions under which various mineral admixtures described above were used, the author will forecast the future of mineral admixtures as follows. Strength, durability and fluidity are among the three important areas of concrete performance. Without any doubt, it is the cement matrix which has the greatest influence on these major characteristics of concrete. Materials affecting the physical properties of cement matrix are cement, mineral admixtures and chemical admixtures. Conventionally, in most cases, mineral admixtures were used with the aim of reducing the concrete price. However, in the future, by-product mineral admixtures will be utilized with the aim of improving concrete performance. Increasing use of new admixtures, such as rice husk ash and ultra-low-heat blends is anticipated, and at the same time, the level of expertise of the engineers who utilize them at the construction site must also be raised.

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TABLE 1 — ANNUAL PRODUCTION AND UTILIZATION RATES OF SILICEOUS BY-PRODUCTS (TONS) (1988, Ref. 5)

	Fly ash x 10^6		Blast-furnance slag x 10^6		Condensed silica fume x 10^3	
Country	Production	Utilization	Production	Utilization	Production	Utilization
Australia	3.5	0.25	4.7	0.12	60	20
Canada	3.3	0.8	2.9	0.2	23	11
China	35	7.2	22	16	None	None
Denmark	1	0.45	None	None	None	None
France	5.1	1.5	10.4	1.9	60	None
Germany (Fed. Rep.)	2.6	2.0	15	2.8	25	None
India	19	0.5	7.8	2.8	None	None
Japan	3.7	0.5	24	8.2	25	None
Netherlands	0.5	0.3	1.1	1	None	None
Norway	None	None	0.1	None	140	40
South Africa	12.9	0.1	1.5	0.6	43	0
Sweden	0.1	0.02	0.1	0.03	10	1
United Kingdom	13.8	1.3	1.5	0.25	None	None
United States	47	5	13	1	100	2

TABLE 2 — CHARACTERISTICS OF SILICA FUME (Ref. 13)

Type / company	Si		FeSi-75%			FeSi-50%		Scancem	Elkem	Iceland	Hanna
	*	**	*	**	***	**	***		G980-960	Alloys	Canada
Chemical composition											
ig.loss	0.8–1.5	2.5	2.0–4.0	2.7	1.7–9.2	3.6	1.7	2–4	1.0–3.0	--	--
SiO_2	94–98	94	86–90	89	69.8–91.6	83	91.0	86–96	95–97	92–94	92–94
Al_2O_3	0.1–0.4	0.06	0.2–0.6	0.4	0.2–1.8	2.5	0.8	0.2–2.2	0.3–0.7	0.61	0.20–0.30
Fe_2O_3	0.02–0.15	0.03	0.3–1.0	0.6	0.6–4.1	2.5	0.6	0.3–2.2	0.2–0.3	0.94	0.10–0.30
CaO	0.08–0.3	0.5	0.2–0.6	0.2	0.1–2.9	0.8	0.2	0.1–0.6	0.3	0.39	0.10–0.50
MgO	0.3–0.9	1.1	1.0–3.5	1.7	0.3–3.9	3.0	1.4	0.3–3.5	0.2–0.5	1.58	0.10–0.15
Na_2O	0.1–0.4	0.04	0.8–1.8	0.2	0.20–2.33	0.3	0.92	0.8–1.8	0.1–0.3	--	0.10–0.20
K_2O	0.2–0.7	0.05	1.5–3.5	1.2	0.80–5.52	2.0	3.04	1.5–2.5	0.5–0.8	--	0.10(Na)
C	0.2–1.3	1.0	0.8–2.3	1.4	0.4–3.3	1.8	0.6	0.5–2.5	0.7–2.5	--	0.10(K)
SiC	0.2–1.0	--	0.1–0.4	--	--	--	--	--	--	--	3–5
SO_3	--	--	--	--	0.0–1.3	--	0.0	0.4–1.5	0.1–0.4	--	0.10(s)
TiO_2	--	--	--	--	0.00–0.03	--	0.00	--	--	--	--
MnO	--	--	--	0.06	0.01–0.51	0.2	0.15	--	--	--	--
Cl	--	--	--	--	--	--	--	--	0.05–0.1	--	--
P_2O_5	--	--	--	--	--	--	--	--	0.1–0.23	--	--
others	0.1–0.5	--	0.5–0.9	--	--	--	--	--	--	--	--
Physical properties											
Specific gravity	--	2.23	--	2.21	2.18–2.66	2.30	2.59	2.3	2.2	2.10	2.02
Surface area(m^2/g)	--	20(BET)	--	15(BET)	14.9–24.2	13.5(BET)	14.3	15–20	20	15–20	--
Ave. Diameter(μm)	--	0.18	--	0.26	--	0.21	--	0.15	--	--	0.1
Moisture(%)	--	--	--	--	--	--	--	--	0.6–0.8	--	--
Retained on 45μm(%)	--	--	--	--	--	--	--	--	0.6	--	--
Pozzolanic activity index(%)	--	100	--	97	--	56	--	--	--	--	--

*:Traetteberg A.: Silica fume as a pozzolanic material, CEMENT, Vol.75, No.3, p.369–376, 1978

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TABLE 3 — COMPARISON OF REFERENCES STUDYING WITH VALIDITY OF SILICA FUME TO IMPROVE DURABILITY OF CONCRETE (Ref. 20)

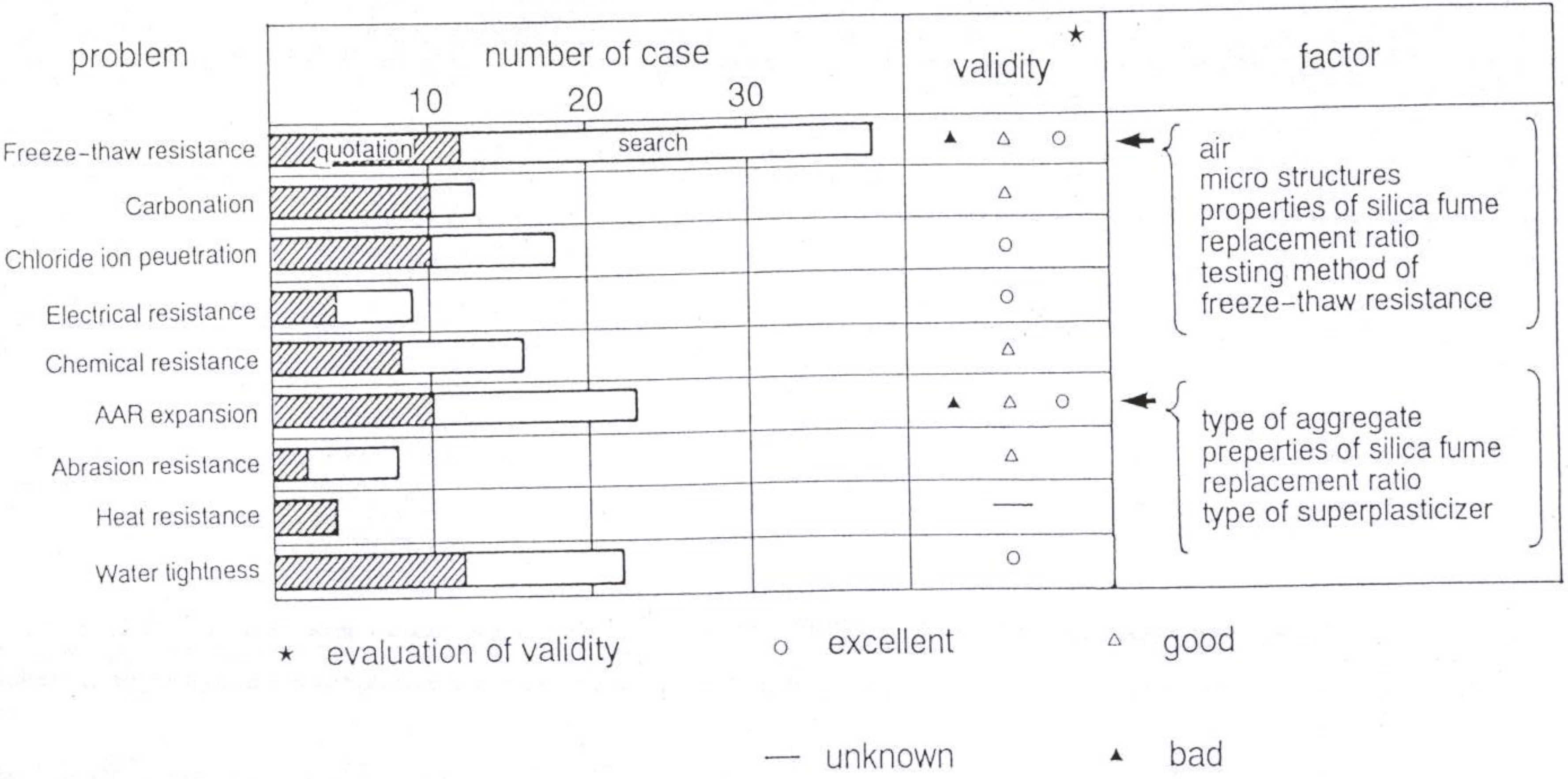


TABLE 4 — EFFECT OF COMBUSTION CONDITIONS ON THE CRYSTAL STRUCTURE AND SURFACE AREA OF RHA (Ref. 25)

Combustion	Hold time	Environment	Properties of ash	
			Crystalline	Surface area, m^2/g
500 – 600°C	1 min	moderately oxidizing	non–crystalline	122
500 – 600°C	30 min	moderately oxidizing	non–crystalline	97
500 – 600°C	2 hrs	moderately oxidizing	non–crystalline	76
700 – 800°C	15 min – 1 hr	moderately oxidizing	non–crystalline	100
700 – 800°C	15 min – 1 hr	highly oxidizing	partially crystalline	6 – 10
> 800°C	> 1 hr	highly oxidizing	crystalline	< 5

TABLE 5 — MIX PROPORTIONS AND PROPERTIES OF FRESH AND HARDENED CONCRETE (Ref. 26)

	Mix proportions* kg/m³					Properties			Compressive strength MPa				Permeability** Coulombs	
Mix No.	C	RHA	C.A.	F.A.	W	W/C	Air %	Slump mm	3d	7d	28d	1yr	28d	1yr
1a (0%RHA)	392	–	1062	786	128	0.33	1.0	200	45	56	65	80	3500	2200
1b (10%RHA)	356	36	1062	786	128	0.33	1.5	225	42	56	77	86	1260	420
2a (0%RHA)	410	–	1044	786	128	0.31	1.0	240	47	60	66	80	3260	2200
2b (15%RHA)	356	54	1044	786	128	0.31	1.5	175	45	60	80	92	870	250
3a (0%RHA)	428	–	1026	786	128	0.30	1.5	225	47	62	70	81	3000	1800
3b (20%RHA)	356	72	1026	786	128	0.30	1.5	200	46	65	80	92	390	190

* : All mixtures contained a constant amount of a superplasiticizer in order to obtain high consistency

** : Coulombs passed in a 6h standard test (AASHO T–227), based on FHWA Report No. RD–81 / 119, Aug. 1981

TABLE 6 — STANDARDS FOR BLAST-FURNACE SLAG IN VARIOUS COUNTRIES (Ref. 29)

Country Code	Japan JSCE Standard	United States ASTM–C 989	U. K. BS–6699	Canada CSA–A 363
Chemical Modulus				
$(CaO+MgO+Al_2O_3)/SiO_2$	min. 1.4	–	min. 1.0	–
insol. (%)	–	–	min. 1.5	–
ig.loss (%)	max. 3.0	–	min. 3.0	–
Sulphide, S (%)	max. 2.0	max. 2.5	max. 2.0	–
Sulphate, SO_3 (%)	max. 3.0	max. 4.0	–	max. 2.5
Magnesium, MgO (%)	max. 10.0	max. 14.0	–	–
Moisture (%)	max. 1.0	–	max. 1.0	–
Retained on 45 μm (%)	–	max. 20	max. 20	–
Blaine (cm^2/g)	min. 2750	–	min. 2750	–
Activity index (%)		(class 80)		
	7d : min. 55	–	–	–
	28d : min. 75	28d : min. 75	–	28d : min. 80
	91d : min. 95	–	–	–
		(class 100)		
	–	7d : min. 75	–	–
	–	28d : min. 95	–	–
		(class 120)		
	–	7d : min. 95	–	–
	–	28d : min. 115	–	–
Flow index (%)	min. 95	–	–	–

TABLE 7 — EFFECT OF FINENESS AND REPLACEMENT (PERCENT) OF BSF ON VARIOUS PROPERTIES OF CONCRETE (Ref. 35)

Fineness (cm^2/g)	2750 – 5500			5500 – 7500			7500 –		
Replacement (%)	30	50	70	30	50	70	30	50	70
Workability	B	B	B	A	A	A	A	A	A
Bleeding	B	B	C	A	A	A	A	A	A
Hydration control	A	A	A	A	A	A	A	A	A
Adiabatic temp. rise	–	–	A	–	–	A	–	–	A
Hydration–heat control	B	A	A	B	B	A	B	B	A
Early age strength	B	C	C	B	C	C	B	B	C
28days strength	B	C	C	A	B	C	A	A	A
Long term strength	B	A	A	B	A	A	A	A	B
High strength	B	C	C	A	B	B	A	A	B
Drying shrinkage	B	B	B	B	B	B	B	B	B
Freez–thaw resistance	B	B	B	B	B	B	B	B	B
Carbonation control	–	–	C	–	–	C	–	–	C
Watertightness	B	A	A	A	A	A	A	A	A
Chloride ion resistance	B	A	A	A	A	A	A	A	A
Ability of seawater	B	A	A	B	A	A	B	A	A
Chemical resistance	B	B	A	B	B	A	B	B	A
Heat resistance	B	B	B	B	B	B	B	B	B
Availability of accelerate curing	B	B	B	B	B	B	B	B	B
Control for AAR expansion	B	A	A	B	A	A	B	A	A

notes
A : superior to OPC (oridinary portland cement)
B : slightly better than or as well as OPC
C : inferior to OPC
– : unknown

TABLE 8 — STANDARD SPECIFICATION OF CONCRETE (HONSHU SHIKOKU BRIDGE AUTHORITY)

Adiabatic Temp. Rise		$K \leq 25$	$T(K) = K \cdot (1-e^{-\alpha t})$
Temp. Rise Coefficient		$\alpha = 0.4–0.8$	
Compressive Strength	7d	≥160kgf/cm^2	·ϕ150 x 300mm cilynder specimen ·water curing
	91d	≥300kgf/cm^2	
Unit Volume Weight		≥2300kg/m^3	·7 days water curing

*Unit weight : C=260kg/m^3, W=145kg/m^3, S=690kg/m^3, G=1200kg/m^3

TABLE 9 — ULTRA-LOW HEAT TYPE CEMENT DEVELOPED FOR MASSIVE CONCRETE (FROM COMMITTEE REPORT)

Plant	Component	Percent of constituent			Type of cement	Specific gravity	Specific Surface cm^2/g	Strength (MPa) (28days)	Heat of Hydration(cal/g) (28days)
		Cement	Slag	Fly ash					
A	3	20	60	20	Moderate	2.65	4530	25	46.7
B	2	30	70	0	Low-heat	2.99	4040	27	48.6
C	2	20	80	0	OPC	2.94	4250	34	55.0
D	3	20	50	27	Moderate	2.75	5520	28	50.1
E	2	10	90	0	OPC	2.89	4400	14	44.6
F	3	16	54	30	OPC	2.63	4580	30	49.0
G	2	18	82	0	Hig early	2.93	4480	26	55.0
H	3	22.5	44.5	33	Moderate	2.70	3660	21	62.0
I	3	25	60	15	Moderate	2.85	3630	32	51.5

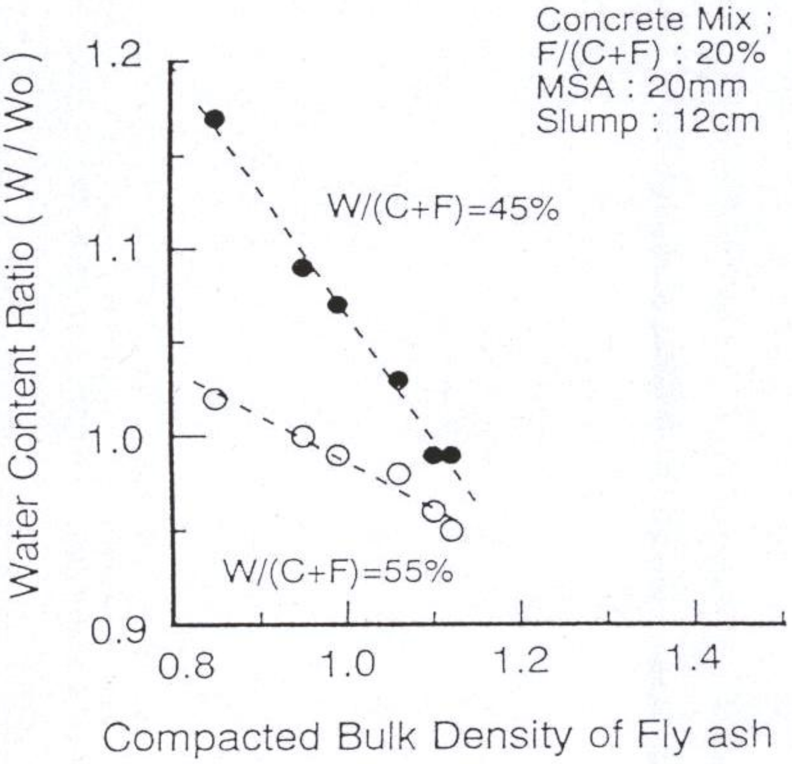
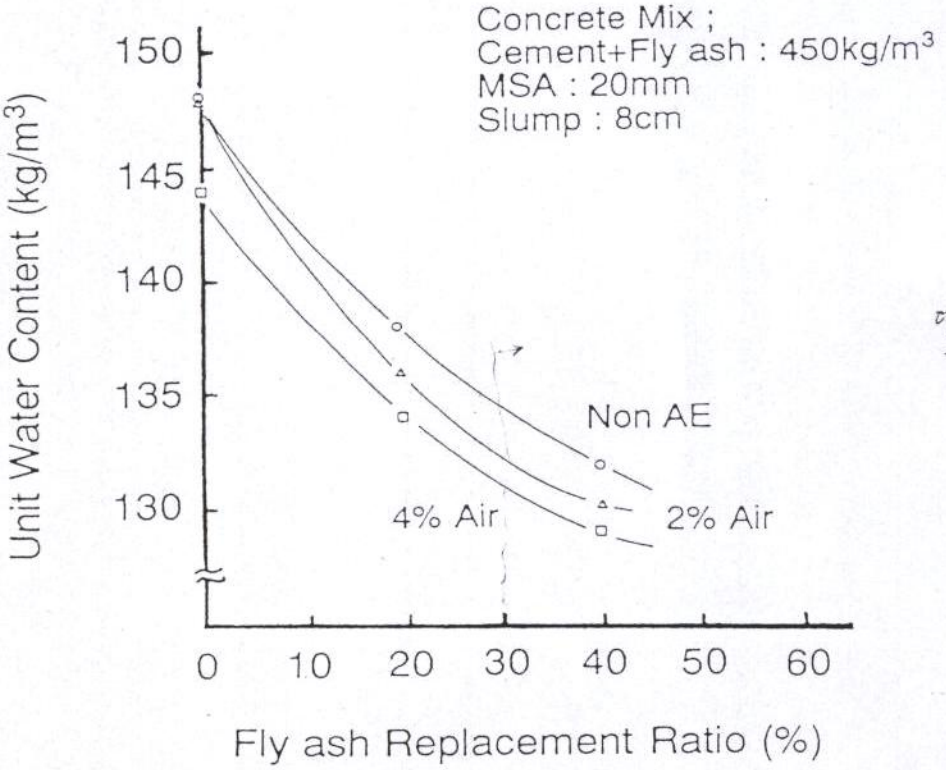
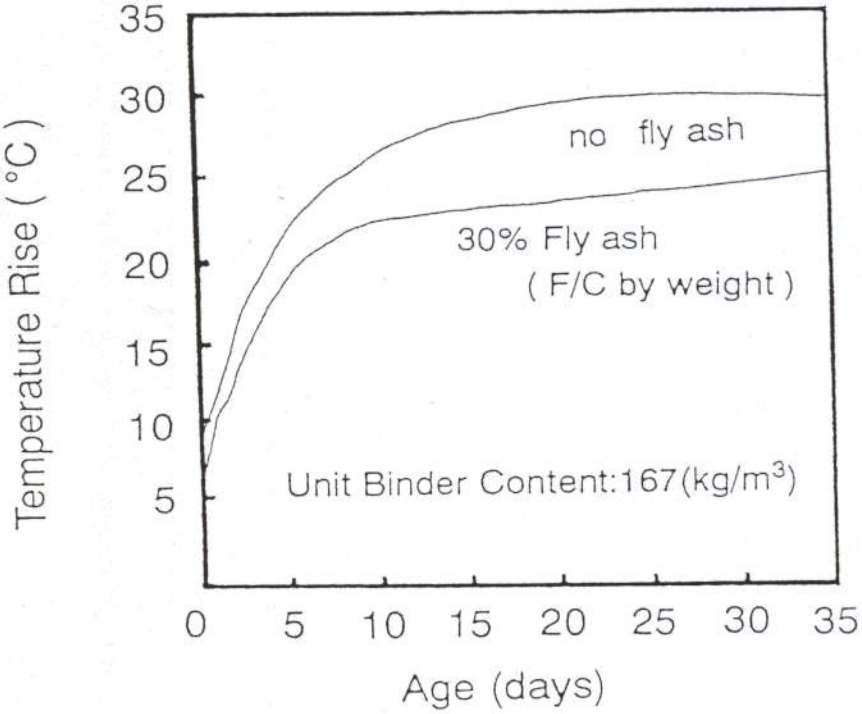


Fig. 1—Effect of compacted bulk density of fly ash on water content ratio of concrete (Ref. 7)



over 30% in
Japan
difficult to
~~[illegible]~~ cure

Fig. 2—Relationship between fly ash replacement ratio and unit water content (Ref. 8)



f.a. is very effective for reducing cracking

Fig. 3—Change in rate of the heat evolution of concrete with and without fly ash (Ref. 10)

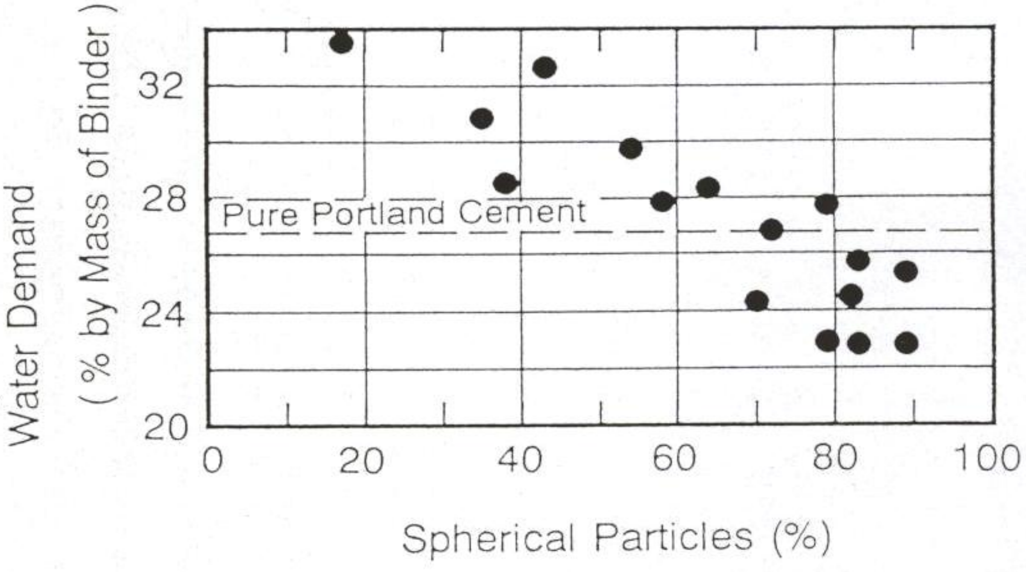


Fig. 4—Influence of spherical particles of fly ash on the water requirement of standard paste: portland cement (70 percent)–fly ash (30 percent) (Ref. 11)

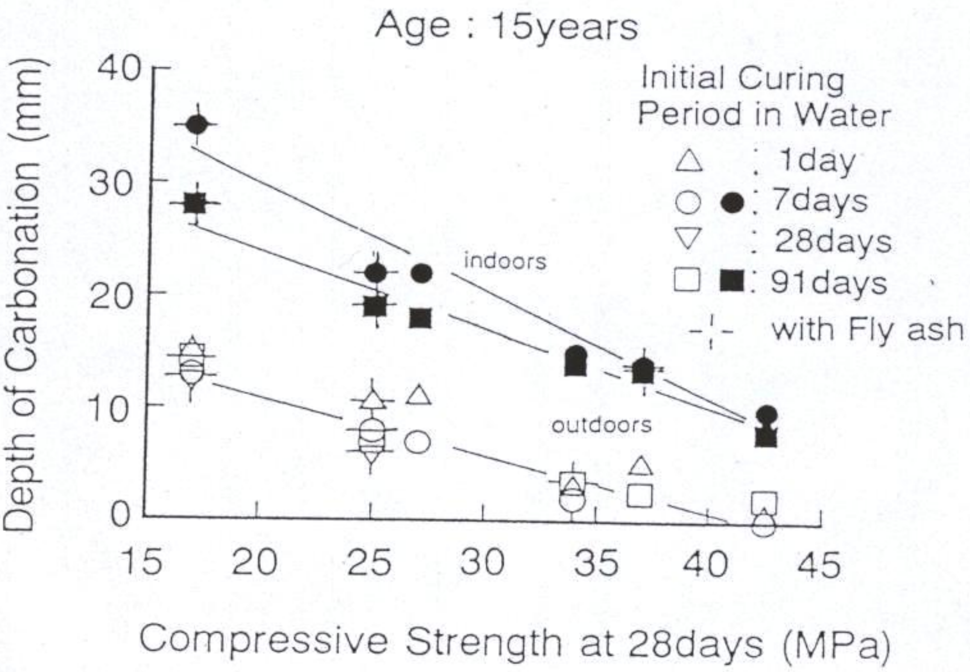


Fig. 5—Relation between compressive strength and depth of carbonation (Ref. 12)

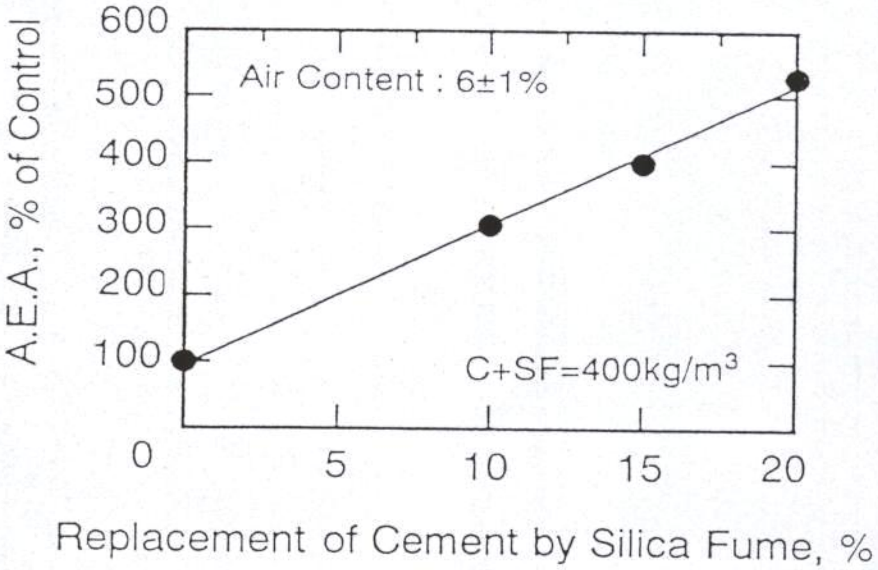
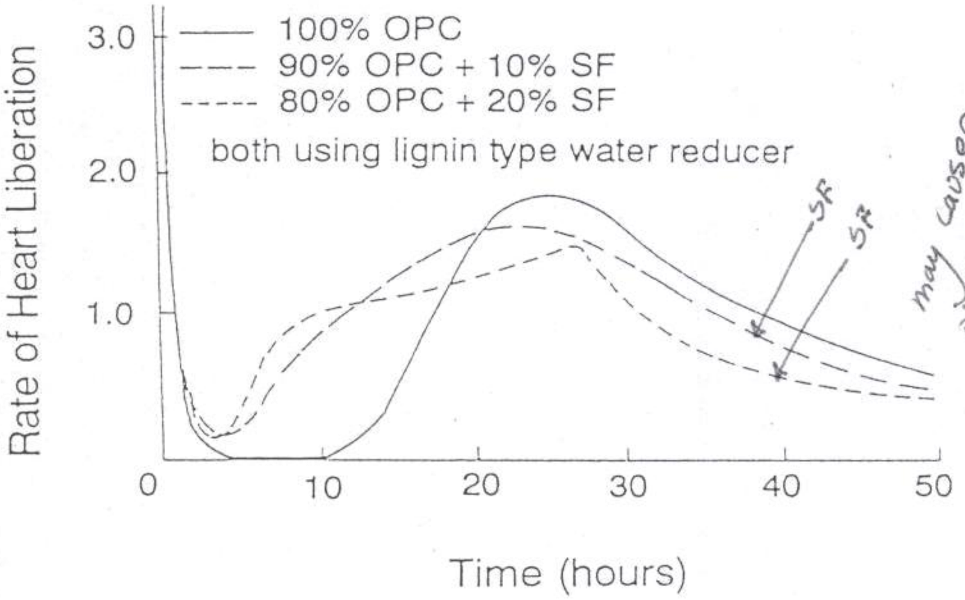


Fig. 6—Effect of replacement of cement by silica fume on the dosage of air-entraining agent (Ref. 15)



may causes plastic shrinkage, wet-curing is necessary.

Fig. 7—Effect of silica fume on change in rate of heat evolution of C/(C + SF) concrete with time (Ref. 17)

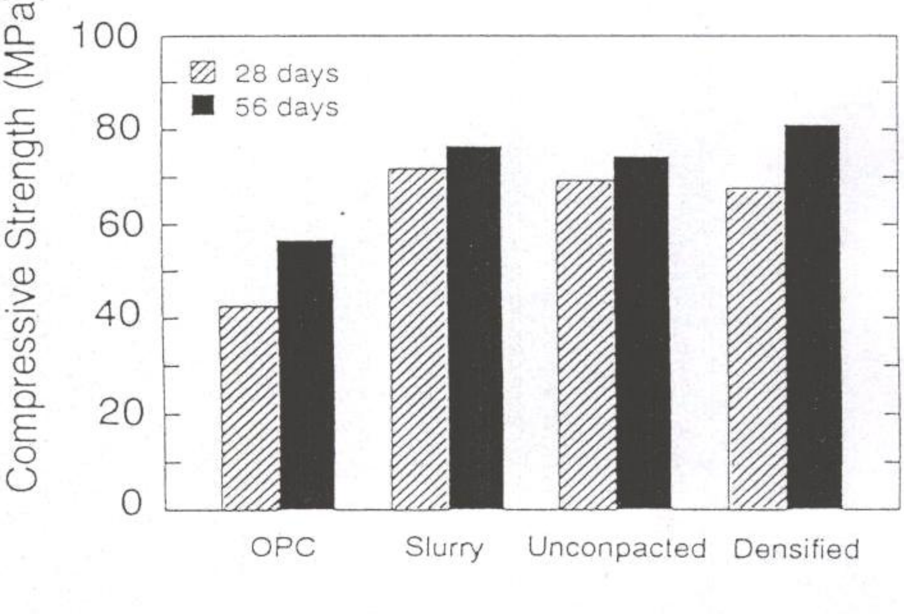


Fig. 8—Effect of the type of silica fume on 28 and 56 days compressive strength of concrete (Ref. 18)

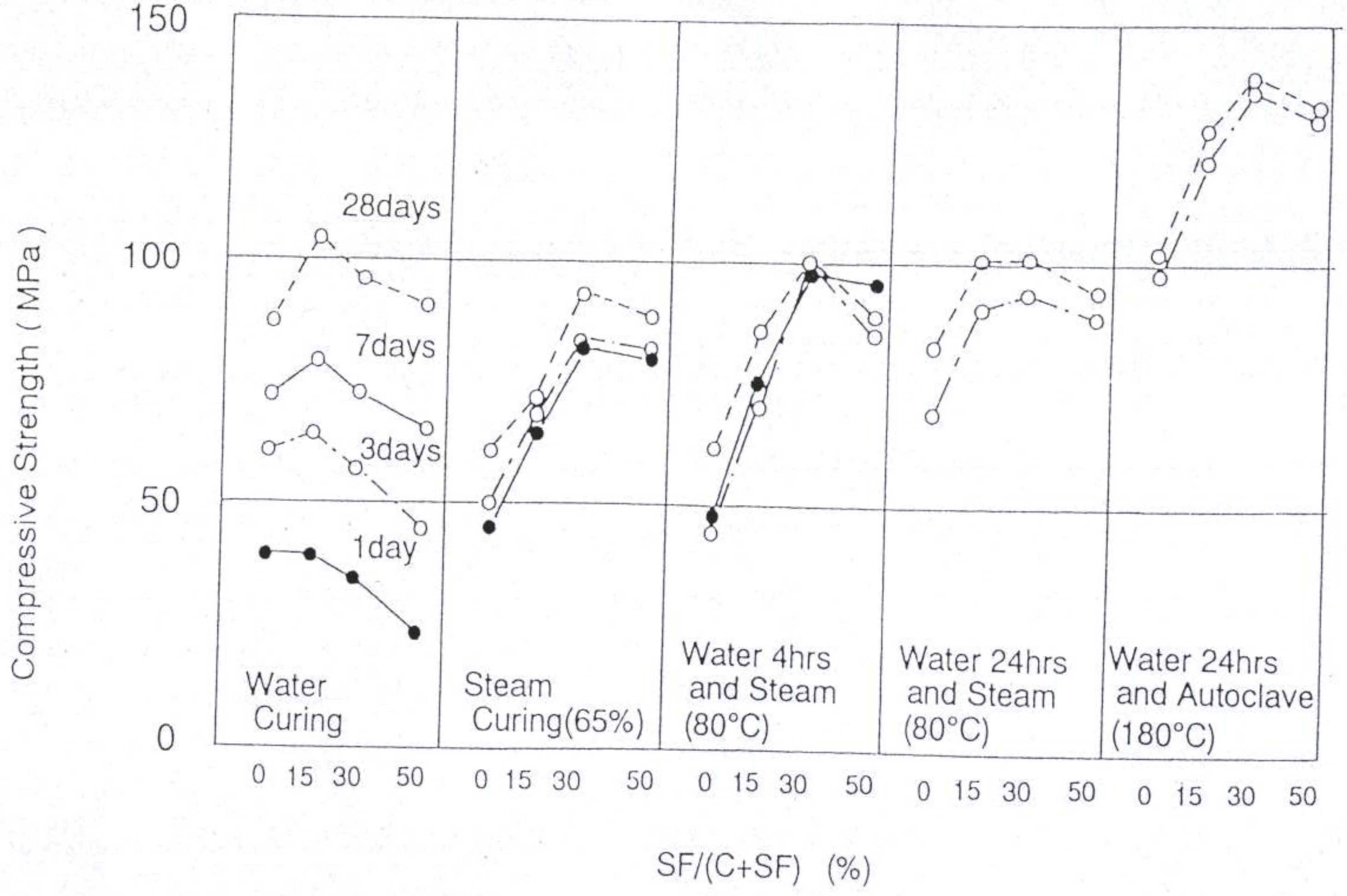


Fig. 9—Effect of silica fume dosage on compressive strength of mortar for various curing conditions (Ref. 19)

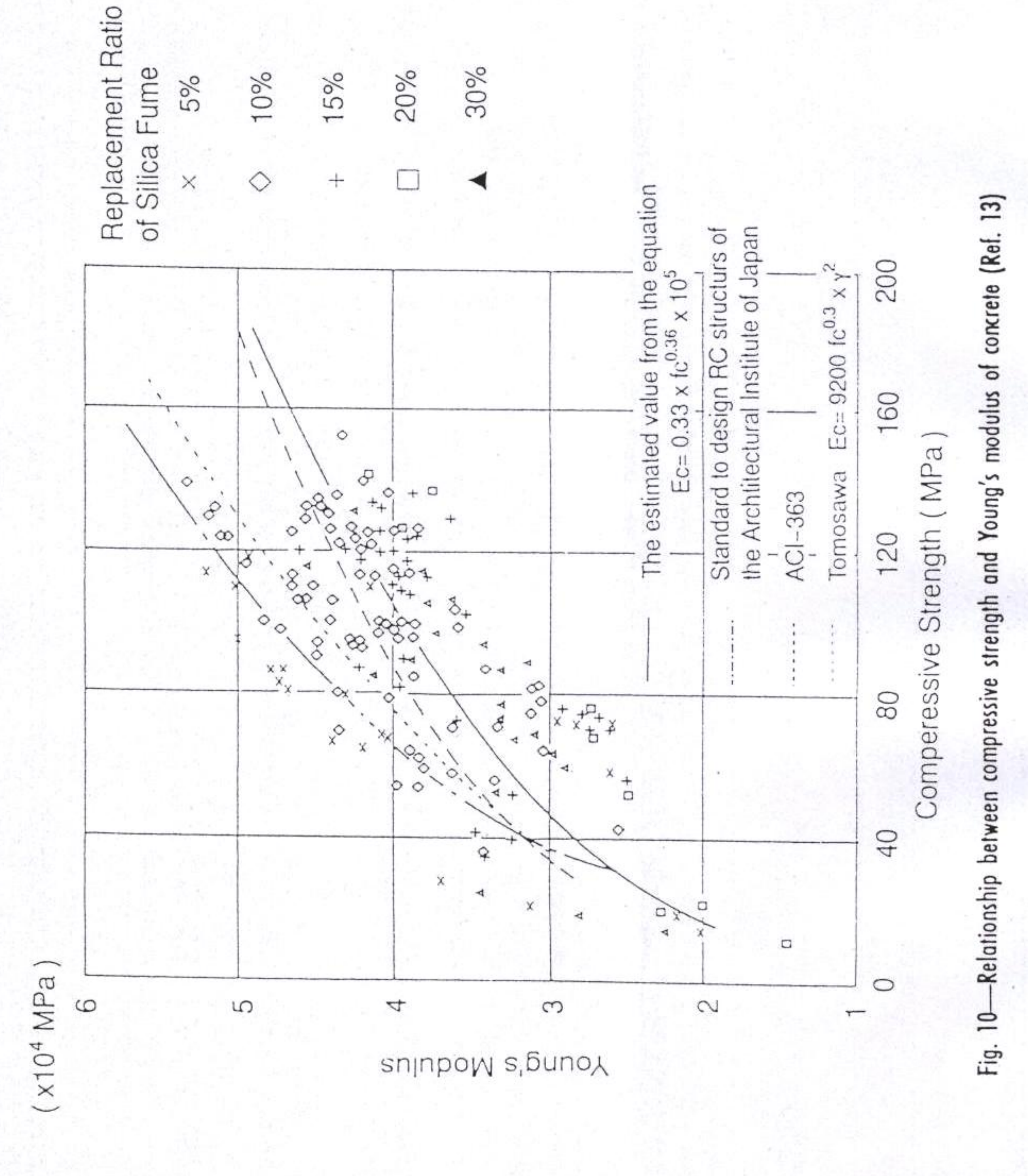


Fig. 10—Relationship between compressive strength and Young's modulus of concrete (Ref. 13)

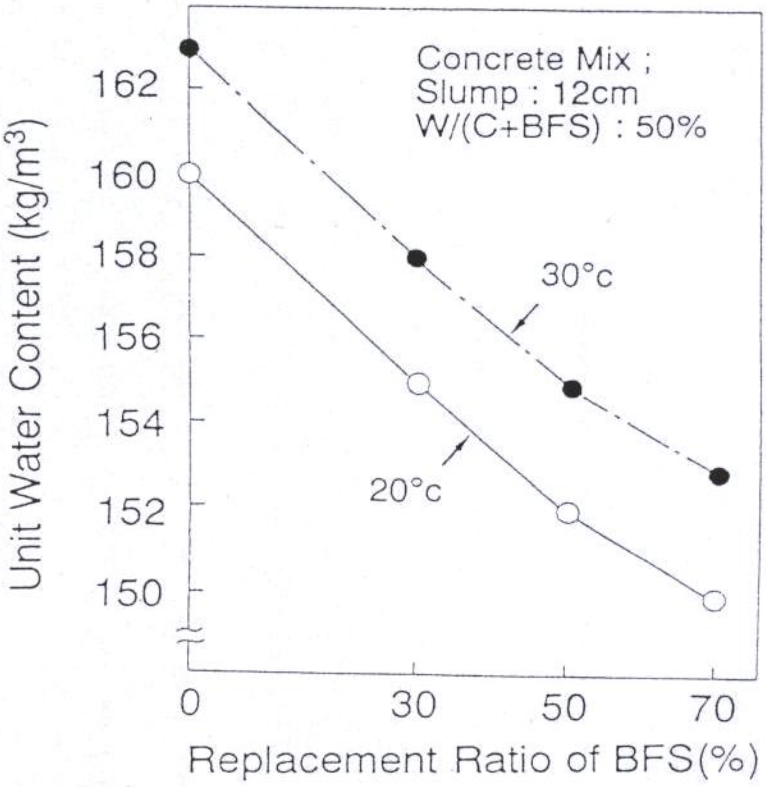


Fig. 11—Relationship between replacement ratio of slag and water content (Ref. 31)

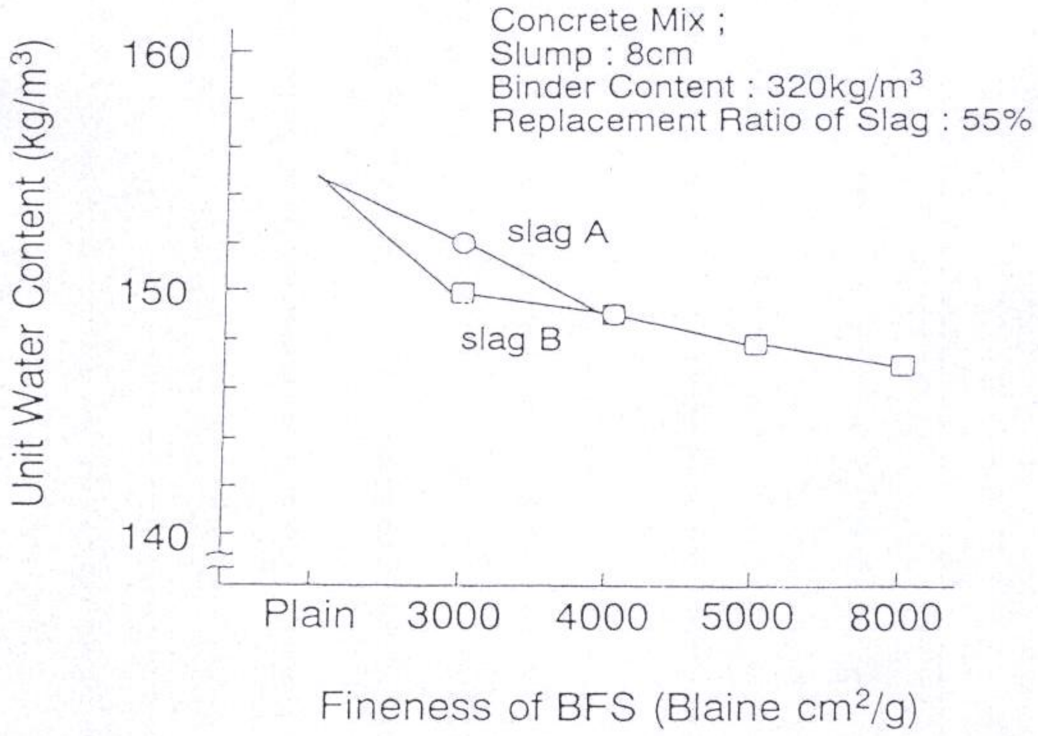


Fig. 12—Relationship between fineness of BFS and unit water content (Ref. 32)

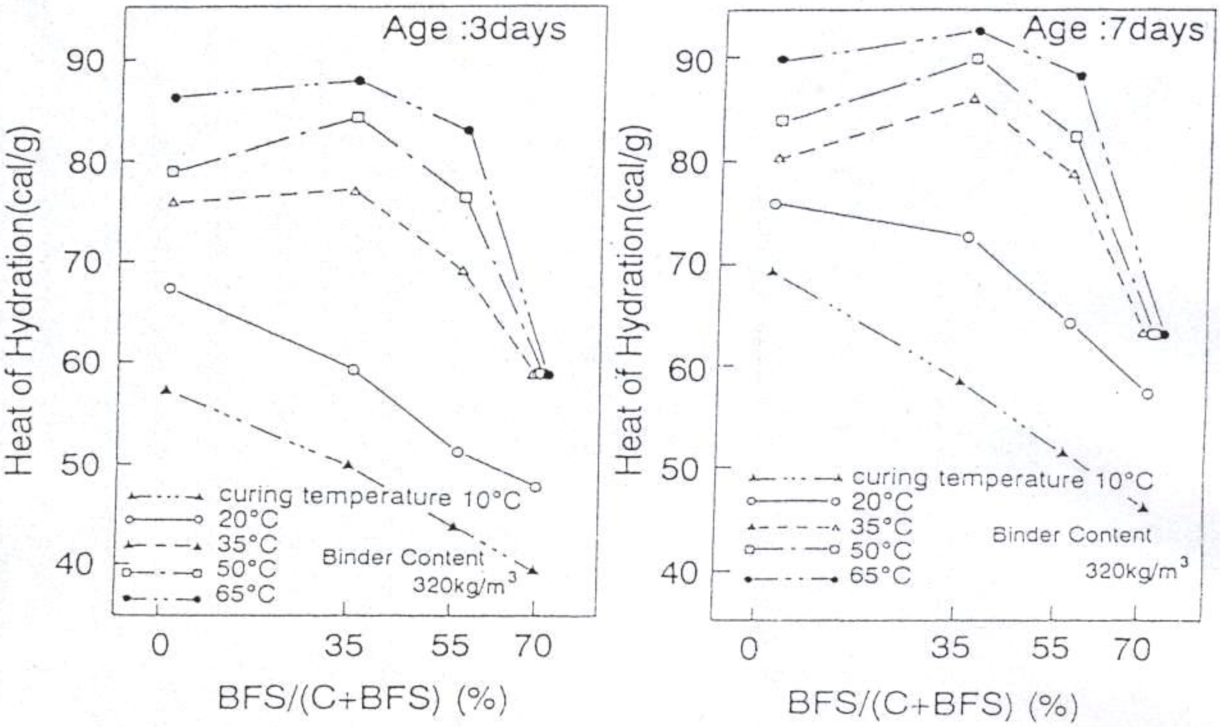


Fig. 13—Effect of BFS on change in rate of heat evolution of concrete at various curing temperatures (Ref. 33)

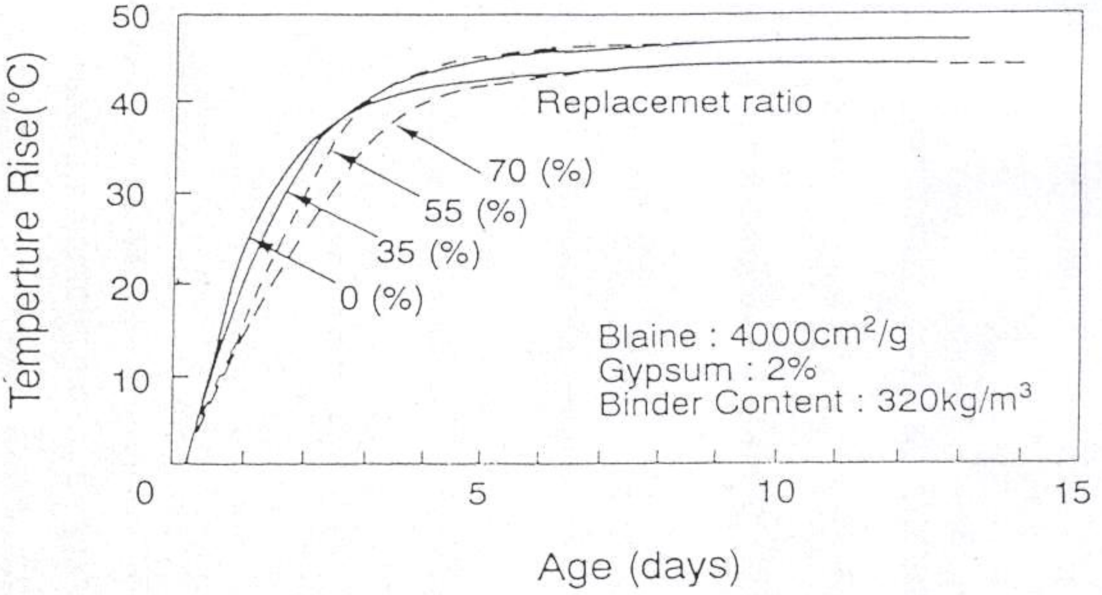


Fig. 14—Effect of slag content on adiabatic temperature rise (Ref. 33)

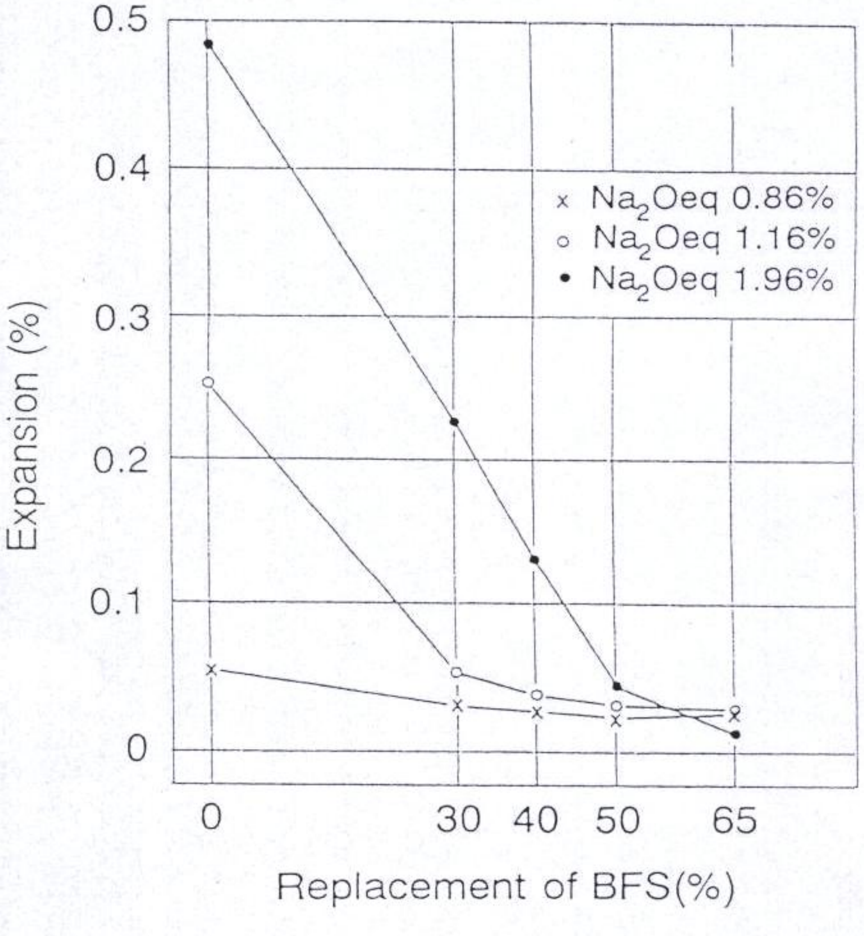


Fig. 15—Relationship between replacement of BFS and expansion due to AAR (Ref. 34)

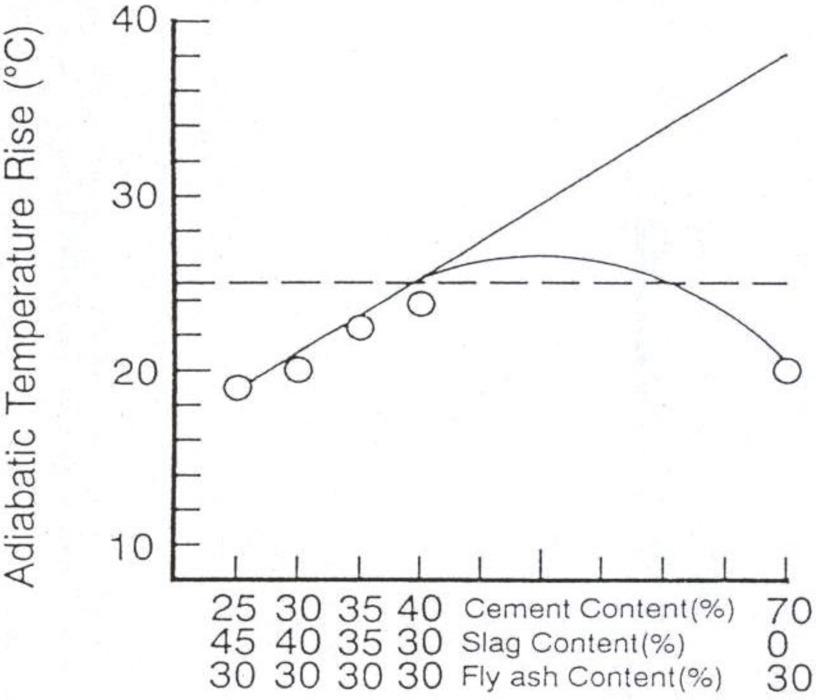


Fig. 16—Relation between Berite type cement-slag-fly ash ratio and adiabatic temperature rise (Ref. 36)

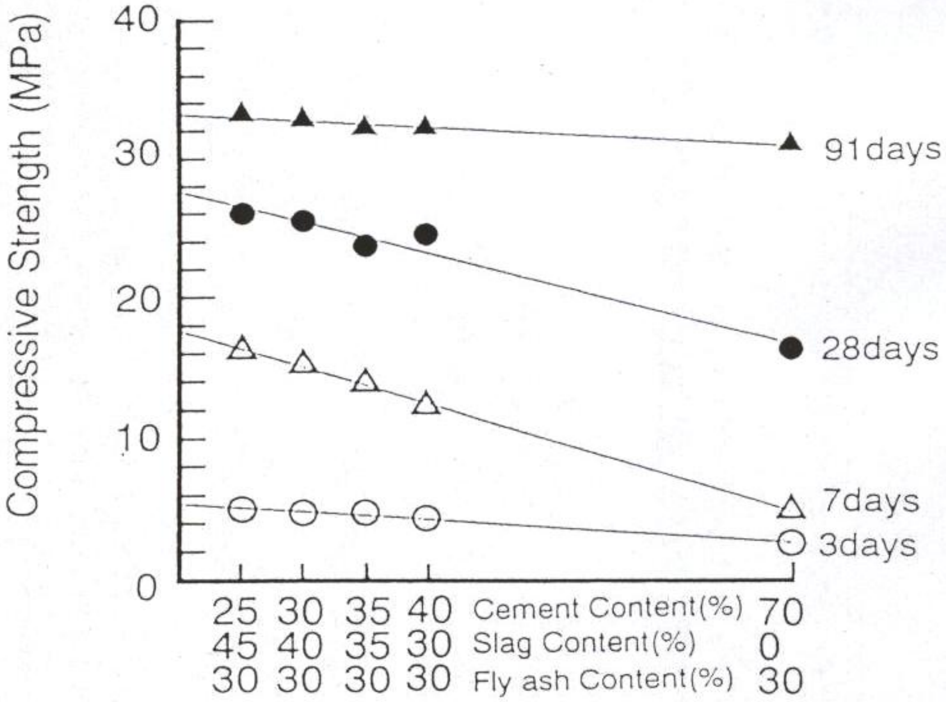
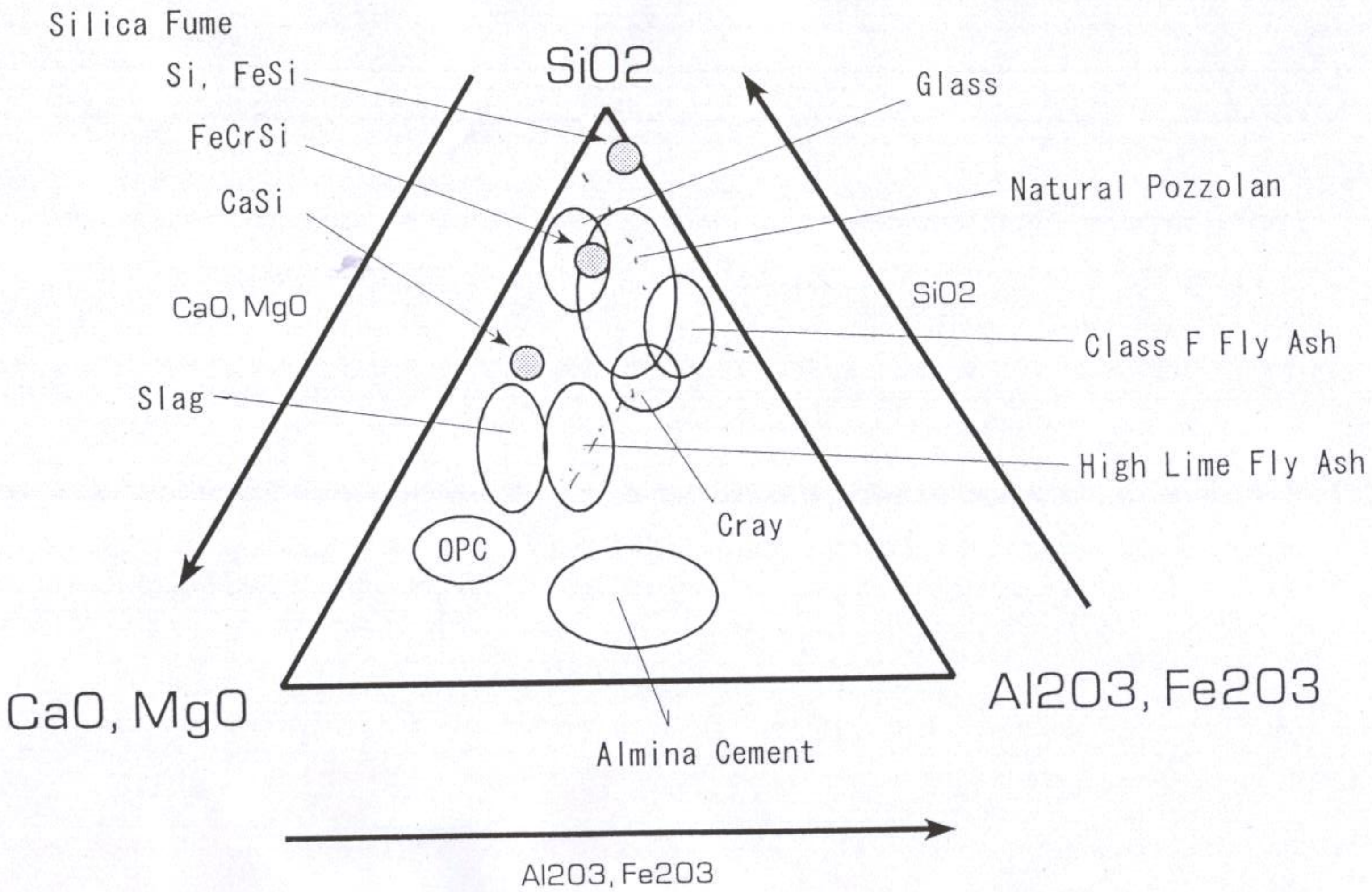


Fig. 17—Relation between Berite type cement-slag-fly ash ratio and compressive strength (Ref. 36)



Classification of Cementitious Materials