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**Autor:** Okada, Kiyoshi

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# Advances Made in Materials Related to Concrete and Applications

Progrès dans les matériaux proches du béton et applications

Fortschritte in der Anwendung von beton-orientierten Zusatzwerkstoffen

**Kiyoshi OKADA**
Professor
Fukuyama University,
Fukuyama, Japan

Kiyoshi Okada, born 1923, received his Doctor of Engineering degree at Kyoto University. Since his graduation from Kyoto University he had been engaged in teaching and research at the same university until retirement in 1986, now is professor at Fukuyama University.

**SUMMARY**
This paper is focused on materials related to concrete and briefly describes the development and application of ultra-high strength concrete, reinforcing fibers, new admixtures and high performance reinforcing bars. And, further, introductory description on polymer-concrete composites is presented. Problems requiring further study is also discussed.

**RÉSUMÉ**
L'article se concentre sur les matériaux proches du béton et décrit brièvement le développement et l'application de bétons à résistance extrêmement élevée, de fibres de renforcement, de nouveaux additifs, d'armatures de renforcement à haute performance. Une introduction est présentée sur les matériaux composites béton-polymère. Des domaines sont indiqués pour des recherches futures.

**ZUSAMMENFASSUNG**
Dieser Beitrag behandelt beton-orientierte Zusatzwerkstoffe, die Entwicklung und Verwendung von Beton höchster Festigkeit, Bewehrungsfasern, neuartige Zusatzmittel, Stähle hoher Qualität und Polymerbeton. Abschliessend werden die Probleme für weitere Forschungsarbeiten besprochen.

## 1. Introduction

A review of the development of structural engineering in modern times will show that the advances made in design and construction of structures have been in step with improvement of existing materials and creation of new materials. The expectations gathered on new materials in today's age of technological revolution are extremely great. Especially, at present, in large-scale technological development such as nuclear fusion and space exploration, and spheres closely related to our livelihood such as microelectronics and medicine, new materials comprise keys to making progress in revolutionizing technologies, and it is said that one who controls materials controls technology. Although the revolutionizing of construction and structural technology is not as spectacular as in the beforementioned fields, the technological background regarding the necessity for developing new materials is the same.

Conventional materials used in structural engineering have mainly been steel, concrete, and on a smaller scale, wood. A new material may be defined as "a material manufactured under close control to draw out a new function not possessed by a conventional material or to greatly improve performance." Of course, new materials will include composite materials that satisfy the demands for more complex, higher-level items that are "lighter, yet stronger," or "more ductile and durable," through combinations of the merits of conventional materials. It should be noted further that for these new matrials to be used practically as supports for advanced technology, it will be necessary to aggressively develop processes for lowering costs and to make strong efforts for promoting practical use.

Development and application of new materials concentrating on cement concrete-related items as sturctural materials will be briefly discussed in theis paper.

## 2. Improving Performance of Concrete

Concrete is one of the oldest artificial materials, is used in a wide range of forms, and today, is still one of the most important construction materials. It is thought that this composite material based on cement will contunue to retain its position as the greatest construction materiral for at least the next half-century while appearing in various new combinations and forms. The features of this mateiral are that its raw materials are abundant and readily available almost everywhere, a little energy is required for manufacturing so that the cost is low compared with other materials, and in additon to such advantages, it has the properties of stability and durability when used as a construction material in various kinds of evironments. However, it is clear as to the properties of concrete that there remains still room left for improvement and higher performance as a construction material, and therefore, besides its use as a general purpose material, concrete is being developed as a material adjusted to be usable under special conditions also.

### 2.1 High-strength Concrete

With the advances made in concrete technology it has become possible for high-strength concrete of compressive strength about 70 to 80 MPa to be produced with comparatively ease. Development of high strength concrete with years is, for instance, as shown in Table 1. This is owed largely to the development of good-quality, high-range water-reducing admixtures, while it is being called for to further develop technology making possible attainment of high strength over around 130MPa without special materials or costs [1] [2]. These high-strength concretes have been put to practical use in individual members and precast products such as piles, but for such concretes to be applied actural cast-in-situ work there must be improvements made in placement techniques and build-up of quality control systems along with progress in concrete manufac-

Table 1 Increase in strength of concrete with years (MPa)

| | Normal | High | Ultra-high |
|---|---|---|---|
| 1950'S | <30 | >30 | - |
| 1960'S | <30 | 30∿50 | - |
| 1970'S | 30∿50 | 50∿100 | - |
| 1980'S | 30∿50 | 50∿100 | >100 |

Table 2 Concrete for CONDEEP SP Gullfaks C

| | |
|---|---|
| Cement (SP30-4A mod.) | 430kg |
| Silica fume | 20kg |
| Sand (0∿5mm) | 920kg |
| Coarse aggregate (5∿20mm) | 860kg |
| Water | 1651 |
| Superplasticizer | 61 |
| Slump | 240mm |
| W/C | 038 |
| Mean 28-d cube strength | 83MPa |
| Standard deviation | 5.4MPa |

turing techniques.

With 1970 as a turing point, there has been much demand for concrete of high strength that can be obtainded by ordinary methods without using special materials such as resins (polymers) or special technologies, and in the Chicago area of the United States, close to 20 buildings have been built since 1972 using concrete columns of compressive strength of 62 MPa as shown before in Table 1. Following this, there have been similar cases in various regions, and according to a recent report, a building using concrete of 131 MPa (age, 56 days) has appeared. [3] In Japan, too, where considerable earthquake resistance is demanded, there are buildings (apartment houses) up to 40 stories including those presently under construction which have employed concrete of compressive strength of 50 to 60 MPa and slump of around 180 mm. There are also many reports of use in members of bridges and other structures, a prominent example being the use in large quantity of high-strength concrete for construction of oil exploration rigs for North Sea oilfield development in Norway. With improvements made in the qualities of materials such as cement, aggregates, and admixtures, concrete of 28-day cube characteristic strength 75 MPa (w/c =0.38, slump = 240 mm, standard deviation 5.4 MPa) is presently being made and placed by pump at the Gullfaks C rig as giving in Table 2. [4] High-strength concrete is usually made with high cement content, low water-cement ratio, ordinary aggregates, chemical admixtures, and pozzolanic admixtures. The mix proportions differ greatly depending on the required strength, age, material characteristics, and place of application. Although there are essentially no fundamental differences from concrete of normal strength with repard to batching, mixing, conveying, placing, and controlling techniques, special consideration is necessary for securing uniform-quality materials to obtain high strength.

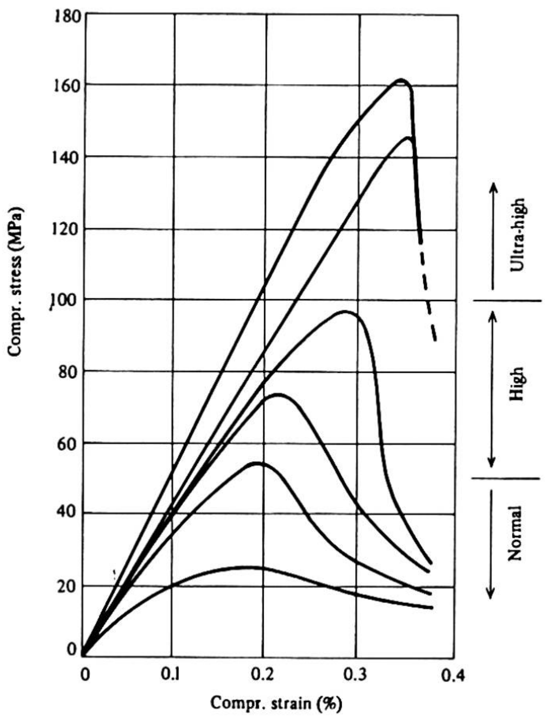


Fig. 1 Stress-strain curves for concretes of various strength

Considering the fact the behavior of high-strength concrete under loading is of slightly brittle nature, as shown in Fig. 1 reexamination is required concerning cross-sectional design, but there are substantial improvements, for example, with regard to reduction in creep and shrinkage, increase in density, etc. [5] It is clearly known, therefore, that the utilization of high-strength concrete to columns which are subjected to vertical forces is quite advantageous economically with respect to reduction in member cross section, early removal of forms, and securing of durability. However, with regard to utilization in beams, it may be said there is room left for study on such as the minimum quantity of tensile reinforcement, the necessity for lateral confinement, etc. from the standpoint of assuring toughness. Furthermore, besides problematic points in construction such as the influence of material characteristics, consolidation and mixing procedures, is is emphasized that there is a necessity for still more study on subjects such as properties of lightweight high-strength concrete and high-strength fiber-reinforced concrete, and application of high-strength concrete in earthquake zones.

## 2.2 Silica Fume Concrete

A substance that is being watched with extremely close attention as a material in making high-strength concrete is silica fume (micro silica). This is a by-product obtained in manufacturing silicon and ferrosilicon alloys and average particle diameters are from 0.1 to 0.2 microns (Specific surface of the order of 20,000 $m^2/kg$). It is an amorphous glassy meterial with $Sio_2$ content generally over 90 percent. Use in concrete was tried for the first time in the 1950s in Norway, and spread rapidly in various parts of the world from 1970. The objective at the beginnig was to reduce cement content in obtaining identical strength, but it may be said that at present the main purpose of using silica fume is the manufacture of concrete possessing high strength and high durability. [6] The main producing countries of silica fume are the U.S.A., the U.S.S.R., Norway, and Canada. The annual production in Japan is around 26,000 Mg (1984).

Since silica fume is non-crystalline and, moreover, ultra-finely-divided, the hydration activity is great and pozzolanic action occurs at an early stage when mixed with cement. Consequently, concrete using this material has good strength gain at the initial stage, and that compressive strength is proportional to the binder-water ratio is the same as with ordinary concrete. Strength gain can be explained by both pozzolanic reaction and by microfiller effect. An attempt has been made using efficiency factor K to show how many times more effect silica fume has over the same quantity of cement. In essence, with W as unit water content, C as unit cement content, Si as unit silica fume content, and K as efficiency factor, water-binder ratio can be expressed as $W/(C + KSi)$. Examples of the values of K obtained for various kinds of strength are given below in Table 3. [7]

Table 3 Values of K

| Curing | Compressive strength | Tensile strength | Flexural strength |
|---|---|---|---|
| Moist curing | 2 - 5 | 3 - 8 | 4 - 16 |
| Dry curing | 2 - 5 | 0 - 3 | 0 - 3 |

The amount of silica fume used is normally between 5 and 10 percent (volumetric ratio) of the cement content, but since it is a finely-divided powder, there is a tendency for water demand to be increased as the addition to concrete is increased, and because of this, it is necessary to use a high-range water-reducing agent to prevent decrease in strength and increase in drying shrinkage. Bleeding of fresh concrete is also greatly reduced. The structural system of silica fume concrete is close-textured and pore diameters are extremely small compared with concrete in general so that there is a trend for resistance to freezing and thawing to be increased, but very little confirmation of this has been done experimentally, and it is thought the effect of improvement by air entrainment cannot be ignored. Since silica fume is an extremely fine powder, tanks, special trailers, special container bags and the like are used in transportation, while in consideration of surer handling and mixing, the material is made into the form of granules or slurry.

It is thought silica fume will attract even more attention in the future because of its special performances as an admixture. However the drawback of this material is that the amount of production is too limited to be used widely.

## 2.3 Fiber Reinforced Concrete

Attempts to strengthen cement mortar and concrete using various types of fibers have been made from a long time ago to improve low tensile strengths and brittle natures which are major drawbacks of these materials, and asbestos-cement products and reinforced concrete are typical examples. Recently, fiber reinforced concrete (hereafter "FRC) using steel bifers, alkali-resistant glass fibers, vinylon fibers, carbon fibers, aramid fibers, etc. have been finding practical use. The properties of various fibers for FRC are given in Table 4.

Table 4 Various fibers used for reinforcing cement concrete :

| Kind of Fiber | | Tensile str. MPa | Mod. of Elasticity GPa | Specific wt |
|---|---|---|---|---|
| steel | carbon | 500~1000 | 195~200 | 7.8 |
| | zinc-galvanized | 500~1000 | 195~200 | 7.8 |
| | stainless | 500~1000 | 195~200 | 7.8 |
| alkali-resistant glass | | 2500 | 75 | 2.8 |
| Carbon | Low elast. (pitch-based) | 800~1100 | 43 | 1.63 |
| | High elast. (Pan-type) | 2000~3000 | 200~400 | 1.7~1.9 |
| asbestos | | 560~ 980 | 84~140 | 2.9 |
| aramid | | 3100 | 75 | 1.39 |
| vinylon | | 900~1500 | 31~ 37 | 1.29 |
| polypropyrene | | 550~ 760 | 3.5 | 1.5 |
| concrete | | 0.5~2.5 | 10~ 30 | 1.0~2.3 |

The forms of reinforcement by fibers are mainly with short fibers for three-dimensional random reinforcement and two-dimensional random reinforcement by direct spraying. Recently, however, there have been research and development works going on where continuous fibers are solidified into deformed bars using various kinds of resin, with these bars employed for uniaxial reinforcement, biaxial reinforcement in mesh or net form, and triaxial reinforcement in truss or lattice form.

FRC with short fibers dispersed randomly in all three dimensions within the cement matrix will have a significantly lower reinforcing efficiency of the fibers mixed in compared with the cases of reinforcement by uniaxial continuous fibers and by short fibers randomly dispersed in two dimensions due to the effects of alignment of the short fibers and the length of fibers (effect of adhesion strength of fibers and matrix).

The present situation is that mass-production techniques for reinforced concrete members using continuous fibers have not yet been established, while two-dimensional random reinforcement by short fibers is limited by the method of spraying. In contrast, when short fibers can be dispersed three-dimensionally in random fashion inside a mixer and the mixture cast and molded in forms in the same way as conventional concrete, the lowness of reinforcing efficiency of the fibers can often be more than offset when the improvement in productivity and other improvements in physical characteristics due to reinforcement are considered. It should be noted here that with the current mixing techniques using mixers, approximately 5 percent (by volume) is the limit to addition of short fibers in cement matrices, workability being impaired extremely and scatter in strength sharply increased at higher rates of addition.

### Steel Fiber Reinforced Concrete

Steel fiber reinforced concrete (SFRC) was first tested in the United States in 1971, with the first large-scale application made in 1973. States of the art and problematic points have been widely reported [8] and, therefore, details will be omitted here. Maximum-size aggregates of 10 to 20 mm are generally used for SFRC, and from the standpoint of workability, mix designs are fairly rich with high sand-aggregate ratio. It has been considered that when steel fibers are added to concretes containing an aggregate with exceeding a maximum-size of 20 to 25 mm, the performances of the resulting concretes would not be favorable. However, examination of the results with smaller-sized aggregates shows that because of high cement content there are drawbacks such as large volume change due to heat evolution and the tendency for cracks to occur readily when cross sections are thick due to shrinkage of cement paste. As a consequence, there are studies being made, in which rather than aiming to reduce unit cement content, while giving consideration to workability, maximum size of aggregate is increased to about 40 mm, aggregate quantity is increased, and in accordance, long steel fibers (made longer than maximum aggregate size to, for example, 50 to 60 mm) are added. Using such fibers, which are hooked or corrugated, concretes having better impact strengths and fatigue strengths have been obtained compared with conventional streight fibers (length, 19 mm). [9]

## Glass Fiber Reinforced Concrete

Details concerning glass fiber reinforced concrete (GFRC) will also be omitted. Through development of alkali-resistant glass fibers started around 1968 in the United Kingdom, use of these fibers has gradually increased, and they are being utilized in various construction materials such as curtain walls and panels, but the alkali resistance of the glass fibers is still not perfect, and this has been an important research topic. To cope with this, it has been attempted to lower the degree of alkalinity in concrete using admixtures such as silica fume and blended cement, while cement for GFRC (calcium silicate-Hauyne-slag-based cement), which does not produce $Ca(OH)_2$ during the process of cement hydration and has very low $OH^-$ ion concentration in the hardened system, has been developed, and good test results have been reported to draw attention. The components in comparison with ordinary cement are shown in Table 5. [10]

Table 5 Chemical composition of GFRC cement

| Cement | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | $SO_3$ |
|---|---|---|---|---|---|
| GFRC cement | 23.2 | 13.8 | 1.1 | 47.5 | 9.3 |
| Ordinary portland cement | 22.2 | 5.2 | 3.1 | 64.8 | 2.0 |

## Carbon Fiber Reinforced Concrete

Carbon fibers for reinforcing cement concrete may be classified into two types-one is pitch-based fibers made from pitch and the other is pan-type fibers made from acrylic fibers. Research on carbon fiber reinforced concrete (CFRC) was first started by M. A. Ali, J. A. Waller and others in the 1970s, and in these studies, pan-type fibers were used, mainly aligned unidirectionally, by which it was shown that high tensile and flexural strengths were obtained in proportion to the fiber content (for example, tensile strength of 50 MPa and flexural strength of 100 MPa with content of 5 percent). [11] However, pan-type fibers are expensive and there have been few cases of practical use. In contrast, research has been done in Japan for development and application of low-cost pitch-based fibers. Successful use in large quantities for highe-strength, high-quality, lightweight cladding tile panels and curtain walls made by mixing short fibers 3 to 10 mm in length and 15 to 20 μm in diameter mixed in mortar at rates of 2 to 4 percent (volumetric) and cured by autoclaving has been reported. For example, in the ARK high rise office building (37 stories) in Tokyo, 5540 lightweight CFRC curtain wall of 1.47 m width, 3.76 m height, and 1 Mg mass were manufactured, in which about 170 Mg pitch-based carbon fiber was used. The tensile stress-strain curves for normal CFRS is, for example,shown as in Fig. 2 [12]

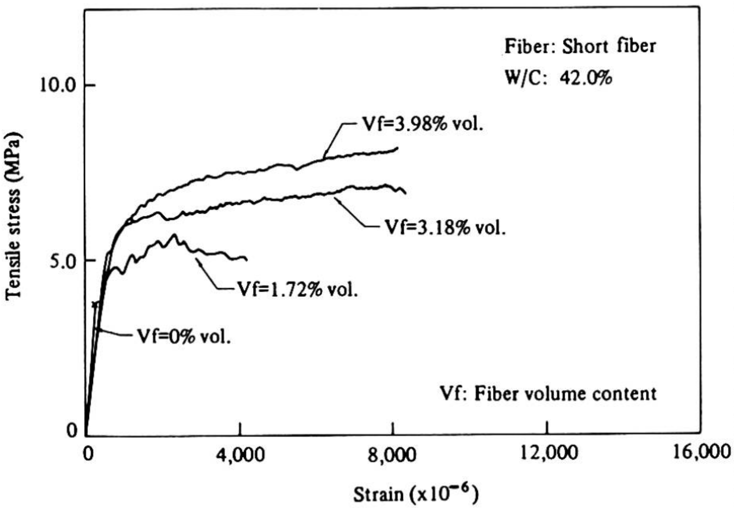


Fig. 2 Tensile stress-strain curves for CFRC.

Aramid Fiber

Aramid fibers possess physical properties intermediate between pitch-based and pan-type carbon fibers. The flexural strength of aramid fiber reinforced mortar is approximately the same as with carbon fibers. This fiber is lower in heat resistance compared with carbon fibers.

Vinylon Fiber

Vinylon fibers indicate physical properties similar to those of pitch-based carbon fibers, but have good bond with cement matrix, and are highly resistant to alkali. The flexural strength of vinylon fiber reinforced mortar is almost the same as that with pitch-based carbon fibers.

## 3. Development of New Reinforcing Bars

In recent years, opportunities for using reinforcing bars of higher strengths and larger diameters have increased as reinforced concrete structures of larger scale and higher stories have come to be designed and constructed. This topic will be considered below together with the development of salt-resistant reinforcing bars required for improving the durability of reinforced concrete structures.

### 3.1 High-strength Reinforcing Steel

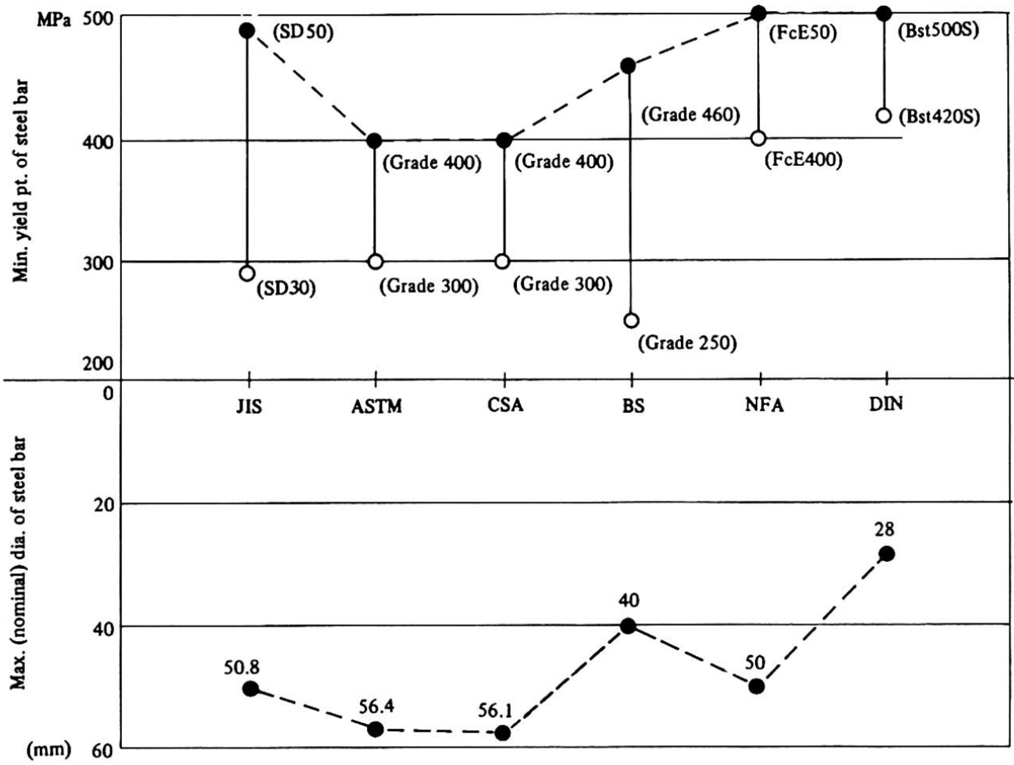


Fig. 3 Min.yield pt. and max. nominal dia. of steel bars specified in various countries.

The limits of minimum yield points of various types of reinforceing bars and upper limits of bar diameters standardized at present in various contries are shown in Fig. 3. [13] The limits to high-strength of reinforcing bars in Japan, Germany, France, and the United Kingdom are around $\sigma_y$ = 50 MPa, while in the United States and Canada they are lower at around 400 MPa.

In Japan, although there is a standard for SD 50 ($\sigma_y$ = 490 MPa), there have been almost no cases of actual use up to now, and practical studies have been with small-diameter bars (diameter: 10 to 16 mm), while concrete strengths have mostly been in a range of 20 to 30 MPa.

There is a limit to high strengh of reinforcing steel that can be effectively utilized in reinforced concrete members. Factors which may be considered to affect the upper limits are the following:

1) Ultimate flexural strengths of beam and column cross sections
2) Flexural ductilities of beam and column cross sections

3) Shear Strengths of beam and column members
4) Bond strength, etc.

In case of using high-strengh reinforcing bars in beams, there may be a limit to the bar stress for the most effective use from the standpoints of limitations in crack width at the serviceability limit state and/or the fatique limit state. In contrast, in application to a column in which the action of axial compressive force is predominant, the problems of cracking limit due to bending moment and fatigue of reinforcing bar due to repetitions of live load are decreased. As a consequence, a large reduction in column cross section becomes possible through the combination of high-strength concrete and high-strength steel of large diameter, and an economic advantage can also be adequately secured. According to recent studies on the use of SD 50 it is shown that the more varieties of designs can be made the higher the concrete strength, and that if adequate shear reinforcement is provided sufficient flexural ductility can be secured for earthquake resistance even when SD 50 is used. Studies also indicate that, sufficient safety can be secured on bond strength so long as excessively large-diameter bars are not used, and moreover, in case cover is made thick correspondingly to bar diameter. In this way, reduction in reinforcing steel quantity and consequential ease of reinforcing bar placement are made possible through the use of SD 50, while for the same flexural strength, reduction in member cross section becomes possible when an equal quantity to low-strength reinforcing bars is used. On the other hand, a kind of deformed prestressing bar produced by induction heat heat treatment of dia. 6.4 to 13 mm having yiels point $f_y$ = 1275 MPa and tensile strength $f_u$ = 1422 MPa can be used for shear reinforcement (including spiral) in beams and columns of building in Japan, although the allowable stress intensity is limited to 196 MPa for service load and 588 MPa for ultimate load (usually earthquake load). These advantages of using high strength bar is to be pursued more, and future developments are looked forward to.

## 3.2 Large-diameter Reinforcing Bars

Utilization of higher Strength as well as larger diameter of reinforcing bars is conceivable for the purposes of manpower reduction, mechanization of reinforcement work and improvement in construction precision in large-scaled reinforced concrete structures. Accordingly, D 57 (#18) has been standardized under ASTM in the United States, and an even larger D 64 (#20) has been developed also in Japan. For this bar, a thread-like deformation along the bar length has been adopted for ease of mechanical jointing. [14] Anchorage of these reinforcing bars is of mechanical type using anchor nuts and anchor plates, the anchoring mechanism of which consist of the bond force of the specified embedment length and the bearing force by the nuts and plates.
Problems in using reinforcing bars of such extremely large diameter may be said to be the following;
1) increase in weight per individual bar, 2) increase in bending radius of reinforcing bar, 3) reduction in joint-forming efficiency, 4) impairment of bond and splitting strength of members 5) impairment of cracking properties of members (increase in crack width).

Because of these problems, development work is going on concerning pre-assembling in placement of large-diameter bars, efficient placing equipment, and sure mechanical joints, along with which experimental studies are being made on mechanical properties of members. Fig. 4 shows examples of the influences of various-diameter reinforcing bars on cracking properties of beams, the dimension of which is 30 x 65 x 120 cm (b x h x I) for small beams and 60 x 130 x 1040 cm for large ones. It has been reported that when using such large-diameter bars, such measures as inserting reinforcing bar grills-steel mesh composed of 10- to 13-mm diameter bars with spacing of 10 to 20 cm, for example, at the cover (10 to 30 cm) - are quite effective. [14]

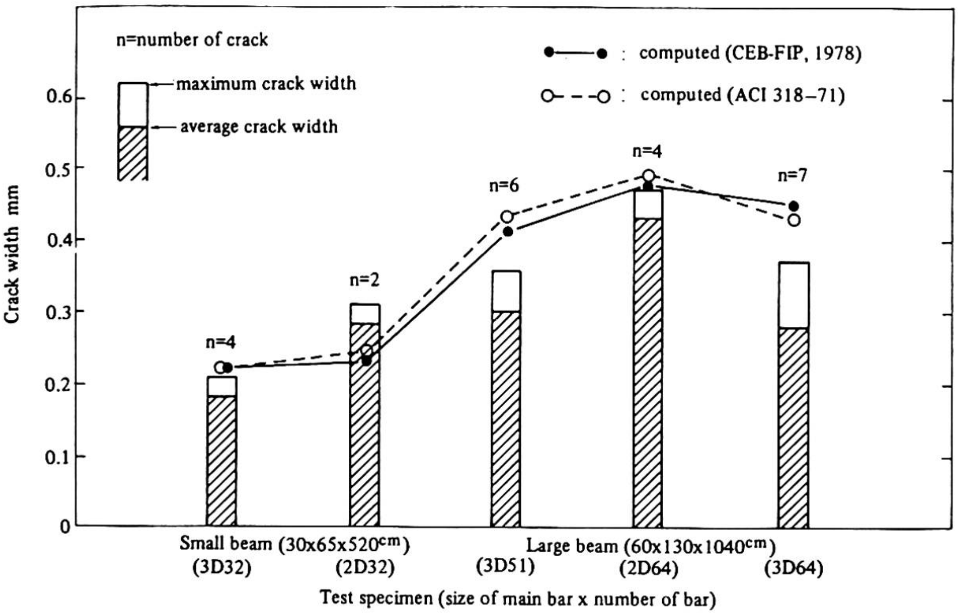


Fig. 4 Comparison of crack width in beams with smaller dia. of bars and those with large ones. ($\sigma_s$=1800 Kgf/cm$^2$, static load)

### 3.3 Salt-resistant Reinforcing Bars

Corrosion of reinforcing bars in concrete has been aggravated by the use of marine sand as aggregate, spreading of de-icing chemicals in winter on the bridge slab, and penetration of chlorides into offshore structures. Since the use of epoxy resin-coated reinforcing bars was started in the United States around 1970 as a measure to prevent corrosion, such bars have come to be used increasingly in the United States, Canada, Middle East countries, Japan, and the United Kingdom, and it is a standard now in 48 states of America for this type of bar to be used in bridges. Such reinforcing bars are made by electrostatic powder coating with coat thicknesses normally 150 to 300 μ, and averaging about 200 μ. It is necessary for care to be exercised concerning lower bond strength with concrete because of the coating, some amount of limitations in bending fabrication of bars, and preventing peeling off of coats during construction. It has also been reported that these bars are approximately double in cost compared with ordinary reinforcing bars, but service life is 10 to 14 times longer. [15]

Meanwhile, several attempts have been made to improve salt resistance through adjustments of the composition of reinforcing steel. That is, salt-resistant reinforcing steels are being developed by selecting appropriate composition systems aiming to impart corrosion resistance several times greater than normal, with rapid corrosion and deterioration not resulting even when carbonation of concrete has occurred, while properties as reinforcing steel such as fatigue resistance, fire resistance, and bond strength are not impaired. As examples, a nickel (Ni) alloy (about 3.5 percent) containing a small amount (not more than 0.3 percent) of tungsten (W), and a 2 percent chromium (Cr) steel have indicated good performances. Exposure tests are being carried out along with laboratory research works and the success of such development research is eagerly awaited. [16], [17]

## 4. New Chemical Admixtures

### 4.1 Superplasticizers

It has been mentioned previously in this paper that the use of a high-range water-reducing admixture is indispensable for manufacturing high-strength concrete containing materials such as silica fume. The use of so-called fluidified concrete made by adding fluidifier to base concrete of comparatively stiff consistency and agitating to increase fluidity with the aim of improving workability of stiff-consistency concrete has been increasing. This method was developed in West Germany and was introduced in Japan around 1975. In Japan the fluidifiers, or superplasticizers as they have come to be called, of naphthalene sulfonate base and others were developed, which were different from the fluidifier (melamine base) of West Germany, and which at first had been used exclusively in building construction on experimental bases, the demand increased in the civil engineering field also. As guidelines on superplasticized concrete were established in 1983 by both the Japan Society of Civil Engineers and the Architectural Institute of Japan, and also recommended practices (draft) were prepared, demand has since increased sharply and the total demand in 1987 is estimated to have been more than 7 million $m^3$ in terms of the volume of concrete.

The rapid increase in the use of superplasticized concrete in Japan had the background described below. In essence, concrete of higher slump came to be used in the architectural field, and especially, with unit water content increased due to use of richer mixes in placing by pump and by the increased use of crushed stone, adverse effects in quality and durability of concrete and structures had been of concern. Consequently, base concrete of medium slump (8 to 12 cm) was fluidified in the field to higher slump (18 to 21 cm) by using a superplasticizer with the objectives being prevention of cracking, reduction of heat of hydration of cement, and improvement of durability through reductions in unit water content and unit cement content. In particular, a principle was set up aiming for unit water content and slump not to be more than 185 $kg/m^3$ and 18 cm, respectively, to secure durability of concrete, and as a result the necessity to use superplasticizers was increased even more. On the other hand, in the civil engineering field, improvements in workability and efficiency have been sought imparting fluidity to conventional stiff-consistency concrete through the use of superplasticizers.

Initially, addition of a superplasticizer to ready-mixed concrete was done at the jobsite in the form of delayed addition and high-speed mixing by agitator immediately before placement. However, because of problems of noise and time-dependent changes in slump after fluidification, the method of adding superplasticizer intermittently to recover slump was devised and a retarding-type superplasticizer with which slump loss is smaller was developed so that the method in which all that needs to be done is to add the superplasticizer at the ready-mix plant is beginning to come into practical use. For example, a certain superplasticizer contains a new, reactive polymer which changes its molecular sturcture in concrete. This polymer is normally a finely-divided powder of several microns insoluble in water which becomes water-soluble affected by the surplus alkali produced as hydration of cement progresses, and functions as a dispersing agent. The result is a gradual supply of dispersing agent making it possible to maintain slump constant as time elapses as shown in Fig. 5. [18] Fluidifying operations are thus simplified for advantages in control so that the use of superplasticized concrete is thought to increase even more. The strength characteristics and durability of concrete fludified in this manner have been studied, and it has been ascertained that they are more or less the same those of base concrete.

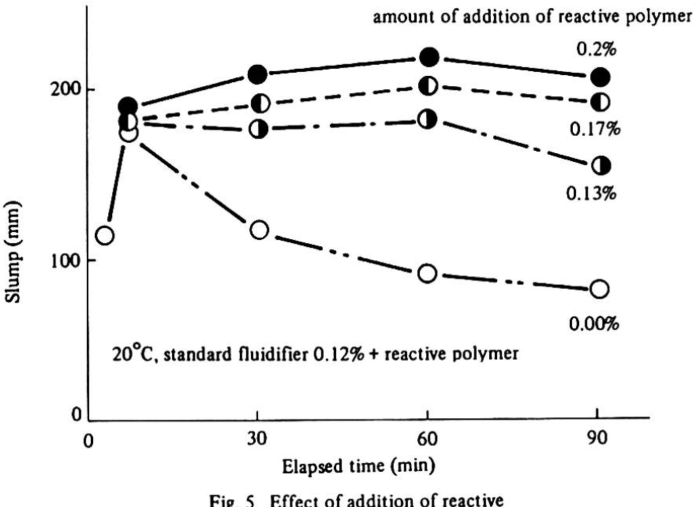

Fig. 5 Effect of addition of reactive polymer on slump

### 4.2 Admixtures for Underwater Concrete

Underwater placemetn of concrete was attempted as early as the mid-nineteenth century, and subsequently, work was done to prevent segregation of materials in water and to secure quality of concrete to satisfy structural requirments, which has evolved in the forms of placement by tremie, prepacked concrete, and development and improvement of equipment. The objects of underwater concrete placement have shifted recently from small-scale of members to offshore platforms, docks and harbor facilities, large-scale of bridge piers, etc. The nuature of underwater concrete has changed from a mere filler material to an important repair material for major underwater structures, properties of which high quality and good durability are demanded. [19]

For this purpose, development work has been going on for special admixtures that are not limited by construction methods and type of equipment used, that keep segregation in water to a minimum and make possible placement of high-strength, durable underwater concrete of increased reliability. The first attempt was made in West Germany in 1977, where an admixture consisting of a water-soluble polymer was added to impart viscosity to concrete making it more difficult for cement and aggregate to become segregated while falling through water. Subsequently, similar development work was done in various countries and these admixtures are being widely used. In Japan, such admixtures have been in actural use since 1981 with approximately 10 products having been made available up to the present for placement of a cumulative volume of approximately 140,000 $m^3$ of special underwater concrete. The results of screening analyses of fresh underwater special concrete and normal concrete are compared in Fig. 6. A design and construction manual for this type of concrete has also been published. [20]

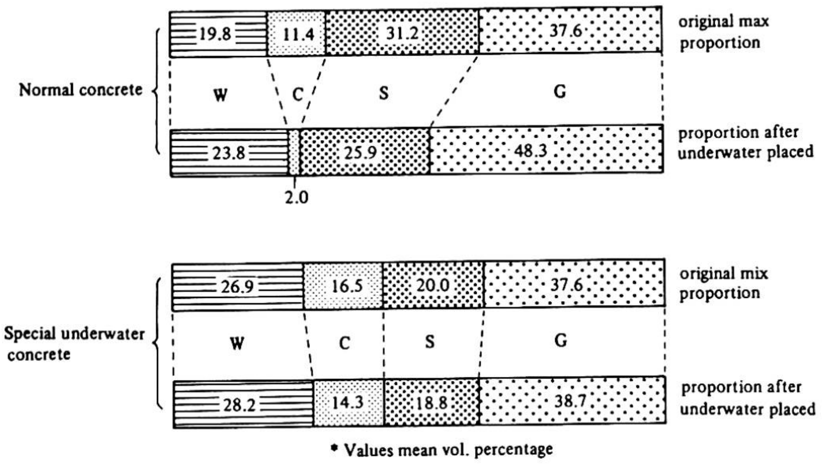


Fig. 6 Wet screening analysis of underwater special concrete and permal concrete

The main components of the special admixtures being used are of two kinds-cellulose base and acrylic base water-soluble polymer. These materials are all either of powder or granular form. The materials are also required to be high in safety when used in under water concrete. The features in quality of special underwater concrete when fresh are as follows:

(i) Excellent resistance to segregation when subjected to washout action of water
(ii) High viscosity and plasticity, and excellent self-levelling and selt-compacting properties
(iii) Little occurrence of bleeding and laitance
(iv) Regarding time of setting, retardation with cellulose base admixture and no change with acrylic base admixture
(v) Increased resistance in case of conveying by concrete pump

When too much amount of special admixture is used there will be objectionable results such as extreme retardation or excessive viscosity for poor workability, and in many cases the admixture is used in combination with an air-entraining agent, water-reducing agent, superplasticizer, etc., and with silica fume, granulated blast-furnace slag, fly ash, and the like. When selecting an

Table 6 Type of Special Admixture and Combination with Superplasticizer

| Special Admixture | Superplasticizer |
|---|---|
| Cellulose base | Melamine sulfonate type (triazine base) |
| Acrylic base | Naphthalene sulfonate |
| | Melamine sulfonate base (triazine) |
| | Acrylic base |
| | Polycarbonic acid base |

air-entraining agent or water-reducing agent, it will be necessary to give consideration to compatability with the special admixture for underwater concrete as shown in Table 6. [20]

4.3 admixture for Highly Durable Concrete

An attempt to greatly improve concrete quality by means of an admixture that has drawn attention is described below.

A certain type of water-insoluble glycol ether derivative greatly reduces drying shrinkage of concrete and shows good durability in relation to permeability, progress of carbonation, and penetration of chloride ions, while an amino alcohol derivative in the constitution of concrete has the functions of absorbing oxygen gas and adsorbing chlorine ions. Taking advantage of these properties and using the two in a suitable combination there is a possibility for a concrete of high durability to be obtained. As an example Fig. 7 shows strengths, drying shrinkages, permeability coefficients, carbonation depths, and chlorine ion penetration depths of mortar and concrete containing 3 percent glycol ether derivative and 1 percent amino alcohol derivative, both by weight of cement, compared with plain or air-entrained concrete. [21] The result show the excellent effect of these admixtures, and it is reported that judging by the rate of increase in carbonation depth it is not a wild dream that concrete of service life longer than 500 years can be made so long as the water cement ratio of concrete is below 50% and the cover of reinforcement is over 40 mm.

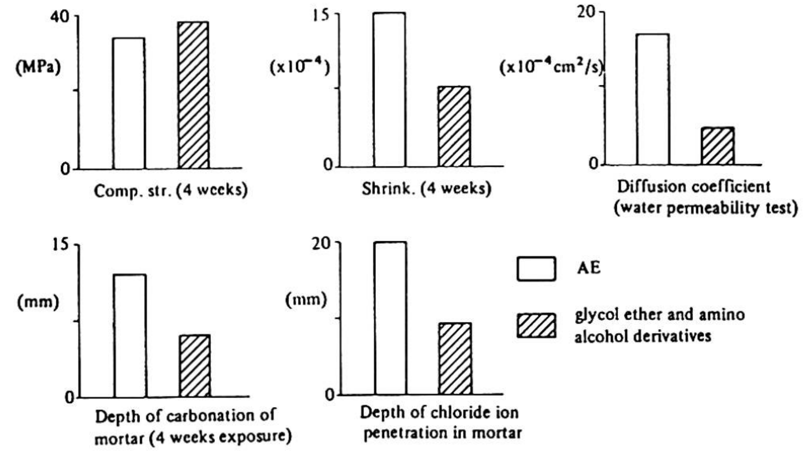


Fig. 7 Durability of concrete containing both glycol ether and amino alcohol derivatives

5. Concrete-Polymer Compositers

It has been approximately 30 years since research and development began on concrete-polymer compositer with the aim of improving the performance of cement concrete. The forms of introducing polymer into concrete may be classified according to the three of a) poymer modified (cement) concrete (or mortar) (PCC or PPCC), b) polymer concrete (PC), and c) polymer impregnated concrete (PIC). The degrees of improvement it performance achieved all differ, but the principal effects of polymer introduction are improvements in mechanical properties of concrete (for example, ratio between compressive strength and tensile strength), watertightness, freeze-thaw resistance, and resistance to chemicals. However, there are some among physical properties which are adversely affected, resulting, for example, in increased thermal expansion and reduced heat resistances.

## 5.1 Poymer Impregnated Concrete

Work on polymer impregnated concrete began from the latter 1960s in the United States, Europe, and Japan, typical monomers for impregnation being methyl metacrylate and styrene. Many results were reported, but research and development on this has not been actively pursued of recent. The reasons are 1) that the menufacturing process is complex and energy consumption in the drying and polymerization processes is large, 2) the performances obtained are not greatly different from those of polymer concrete (resin concrete), and a balance between performance and cost is unobtainable, and 3) methods of measuring poymer impregnation ratio and depth are not available to make quality control difficult. The last and largest case of application in the United States was a road at Grand Coulee Dam, and the construction cost was $51/m$^2$ (1982). [22] However, concrete of ultra-high strength, 196 to 275 MPa in terms of compressive strength was developed in the 1970s through the application of impregnation techniques, while compressive strengths of 225 to 255 MPa have been obtained experimentally through the addition of silica fume and superplasticizer, autoclave curing, and polymetacrylate methyl impregnation. However, these high-strength products have not found practical use as yet. With regard to application of on-site polymer impregnation methods, there have been experiments made with the purposes of improving surface hardness and strength, watertightness, chemical resistance, chlorine ion penetration resistance, and carbonation resistance of existing structures, with work done in repairs of pavements and dams, and corrosion protection of factory floors, but practical applications are still insufficient.

## 5.2 Polymer Modified Cement Concrete (or Mortar)

In manufacturing polymer modified cement concrete (or mortar), polymer is added in the form of a dispersion (latex or emulstion) to ordinary cement concrete (or mortar) at the time of mixing. Polymer dispersions widely used in Japan are SBR (styrene-butadiene rubber) latex, and EVA (ethylene vinyl acetate) and PAE (polyacrylic ester) emulsions, annual consumption exceeding 100,000 Mg. In the United States and Europe, water-soluble polymers such as unsaturated polyester resin are used fairly widely, but these are rarely used in Japan because of high prices. In general, polymer-cement ratios used are in a range of 5 to 30 percent. When polymer-cement ratio is increased, tensile and flexural strengths, extensibility, adhesion, watertightness, chemical resistance, etc. are improved, but surface hardness is reduced. As an example, the increases in resistance of polymer modified cement concrete (mortar) to penetration of chlorine ions ($Cl^-$) are shown in Table 7. [23] This indicates that the use of polymer cement modified concrete is effective for prevention of salt damage to reinforced concrete structures, and this type of concrete is being applied in repairs and overlays of bridge decks deteri-

Table 7 Apparent chloride ion diffusion coefficient of latex-modified mortars and concretes

| Type of mortar | Polymer-cement ratio, percent | Apparent chloride ion diffusion coefficient, $cm^2/s$ | Type of concrete | Polymer-cement ratio, percent | Apparent chloride ion diffusion coefficient, $cm^2/s$ |
|---|---|---|---|---|---|
| Un-modified | 0 | $6.4 \times 10^{-8}$ | Un-modified | 0 | $2.2 \times 10^{-8}$ |
| SBR-modified | 10<br>20 | $6.4 \times 10^{-8}$<br>$3.9 \times 10^{-8}$ | SBR-modified | 10<br>20 | $1.9 \times 10^{-8}$<br>$9.3 \times 10^{-9}$ |
| EVA-modified | 10<br>20 | $4.4 \times 10^{-8}$<br>$2.4 \times 10^{-8}$ | EVA-modified | 10<br>20 | $7.9 \times 10^{-9}$<br>$1.0 \times 10^{-8}$ |
| PAE-modified | 10<br>20 | $3.8 \times 10^{-8}$<br>$4.4 \times 10^{-8}$ | PAE-modified | 10<br>20 | $6.2 \times 10^{-9}$<br>$5.8 \times 10^{-9}$ |

orated by de-icing salts and of parking structure floor slabs.

Since the physical properties of polymer itself are greatly dependent on temperature, the temperature dependence of polymer modified cement concrete is prominent, and it may be considered that the temperature limit for use is approximetely 150°C. According to outdoor exposure tests, it appears that the weather resistance of Polymer modified cement concrete (or mortar) is not of concern for practical purposes. Polymer modified cement concrete has the merit that ordinary concreting techniques can be applied without alteration, but there is little use for it as concrete per se. Applications are as pavement material, floor material, repair material, corrosion protection material, and adhesive material, and it is looked forward to that uses will be expanded hereafter.

### 5.3 Polymer Concrete (Resin Concrete)

Various liquid resins are used as binders for poylmer concrete, but what are most common are epoxy resin, unsaturated polyester resin (polyester-styrene base), and methyl metacrylate (MMA) (monomer). Besides the above, furan, urethance, polyester amid, and vinyl ester are also used. Although differing according to circumstances in the individual countries, MMA and plyester are the lowest in cost. Polyester used is mostly for precast factory products, but MMA is also often sold generally in prepackaged form. This is because of the flammability and disagreeable odor of MMA.

In case of using polymer concrete for structural purposes, steel bars for reinforced concrete, prestressing steel rods, and FRP rods are used for reinforcement of members, while for reinforcement of polymer concrete itself, reinforcing materials such as steel fibers and glass fibers are used. In general, the amount of polymer contained as binder is 9 to 25 wt%. The properties of polymer concrete depend to a great extent on the type and properties of the binder and the properties of aggregate. Manufacturing of polymer concrete (mortar) is done using batch-type forced-mixing mixers and continuous-mixing type mixers. In the United States, a continuous-mixing mixer with capacity of 250 kg/min for repair and overlay of bridge decks has been developed. The advantageous points of polymer concrete for overlays are the good adhesion to old concrete, the feasibility of finishing to thin cross sections (to about 13 mm) for low dead weight, the unnecessity to place approach slabs, the good mechanical properties, and the shortness of curing time.

A noteworthy application of PC is the development in Japan of a method used for automatic construction of small cross-section shield tunnels (inside diameter 120 cm, thickness 10 cm) having lengths of 107 m and 200 m. The compressive strength of specimens cored from lining concrete was 88.9 MPa with standard deviation of 11.4 MPa. [24] The strength of reinforced plastic composite pipe using polyester mortar was comparable to steel pipe with maximum diameter attained as much as 5.2 m. The production is 30,000 to 40,000 ton annually. Other than the above, a recent trend is that which takes advantage of the excellent vibration damping properties of polymer concrete for use in machine tool beds and fabrication of machinery parts, West Germany and Switzerland having taken the lead in development.

## 6. Closing Remarks

The advances in new design and construction of structures have been made together with the development of new materials and improvement of existing ones. In the field of construction, what are required of construction materials are the capabilities to be made into large size and fill large-volume demand, be of high strength, satisfy demands for durability over a long term in a man-made environment, and be of favorable benefit-cost ratio. For such objectives, fundamentally steel and concrete will continue to comprise the mainstream of structural materails, with new varieties respectively developed. This paper has been centered on concrete and briefly describes the development and application of new admixtures, high-performance reinforcing bars, and further, polymer concretes as means of making concretes of high performance. Probelms requiring further study have been discussed, and the necessity for mutual cooperation between construction engineers and materials engineers has been pointed out.

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