Research and application of micro-bead ultra-high performance concrete

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Abstract. Micro-bead is an ultra-fine fly ash of spherical vitreous with an average particle size of no more than 1.2 μm. In this paper, the physicochemical properties of micro-bead, the preparation method of micro-bead ultra-high performance concrete (MUHPC) were described. Furthermore, the characteristics and slump-loss retarding of fresh MUHPC, the strength and durability of MUHPC and the change of mechanical properties and fracture characteristics of MUHPC after incorporating fiber were studied. Results indicated that UHPC with the cement–micro-bead–silica powder as the main binder and incorporated with the appropriate water reducer had a strength reaching up to 150 MPa and a plasticity reaching up to 3 h and no bleeding segregation phenomenon. The C120 UHPC has a low Cl− diffusion coefficient and is resistant to freeze-thaw damage and has a high durability. And for the C120 UHPC incorporating polypropylene fiber, as the fiber content increased, the fracture energy, the brittle characteristic length and the toughness of the concrete all increased. C120 concrete has been applied in the Jingji Building in Shenzhen and the East Tower project in Guangzhou and the pumping height is 500 m or more.

1. Introduction
UHPC is defined as a kind of concrete incorporating fiber or fiber web, has a higher strength and durability than HPC and a compressive strength of more than 120 MPa at 28 days [1]. UHPC combined into self-compacting concrete (SCC) is also a new type of concrete which has supper high strength, high durability and good construction properties [2].

Judicious choice of chemical and mineral admixtures can reduce the cement content and result in economical HPC [3]. When micro-bead was incorporated into concrete as a replacement of cement, the water consumption of concrete would be reduced, and the fluidity, strength and durability of concrete would be significantly improved [4].

UHPC pushes concrete technology to a new height in terms of strength and durability [5]. In this paper, the workability, deformation performance, strength and durability UHPC with micro-bead, polypropylene fiber or other special materials will be studied.

2. Characteristics of micro-bead

2.1. Scanning electron microscopy (SEM)
As shown in figure 1, micro-bead is a spherical glass bead with a maximum particle size of 1.45 μm and a minimum particle size of 2.38 nm.
Figure 1. Scanning electron microscopy images of micro-bead.

2.2. Average particle size distribution

The micro-bead with an average particle size of no more than 0.2 μm accounted for 27.23%, 0.2-1.0 μm accounted for 42.43% and no more than 1.0 μm accounted for 69.66%.

The cement with a specific surface area of about 4000 cm²/g had an average particle diameter of about 10-20 μm. The SF with a specific surface area of about 2000000 cm²/g has an average particle diameter of about 0.1 μm. As the average particle diameter of the micro-bead is no more than 1.0 μm, in the composite powder of the three components of cement, micro-bead and SF, the micro-beads fill the pores between the cement particles, and the SF particles fill the pores between the micro-beads to obtain a densely packed powder.

2.3. Chemical compositions of micro-bead

The chemical compositions of micro-bead are shown in table 1. It can be seen from table 1 that the main chemical composition of micro-bead is SiO₂ and Al₂O₃ with a total content of 83%, the soluble silicon is about 8.67% of the total silicon, the soluble aluminum is about 15.42% of the total aluminum, and the soluble iron is about 3.49% of the total iron. Therefore, the chemical reactivity of the micro-bead is high.

| SiO₂ | CaO | MgO | Al₂O₃ | Fe₂O₃ | Na₂O | K₂O | SO₃ | Carbon content |
|------|-----|-----|-------|-------|------|-----|-----|---------------|
| 56.5 | 4.8 | 1.3 | 26.5  | 5.3   | 1.4  | 3.3 | 0.7 | <1            |

2.4. Loss on ignition

The loss on ignition of micro-bead was about 1.5%, which meet the product quality requirements.

2.5. Standard water demand ratio

The test method and mix proportions are shown in table 2.

| Cement | Micro-bead | Standard sand | Water requirement |
|--------|------------|---------------|-------------------|
| Reference sample | 250 | \ | 750 | Fluidity 130-140 mm, water requirement 110-113 |
| Contrast sample | 175 | 75 | 750 | Fluidity 130-140 mm, water requirement 115 |

When the content of micro-bead was 30% and the fluidity of the paste was 130-140 mm, the requirement was about 98 g. According to the calculation formula: the standard water demand ratio of the micro-bead was 98/115*100%=85%.

2.6. Strength of the paste
The pastes in which the cement was partially replaced by 15%, 20%, 25% and 30% micro-bead were cast according to the cement mortar test method [6] and standardly cured to 28d. The flexural strength and compressive strength of the samples were tested and the results are shown in Table 3.

| Group | Micro-bead content | Flexural strength | Compressive strength |
|-------|--------------------|-------------------|---------------------|
|       |                    | 1     | 2     | 3     | Average | 1   | 2   | 3   | 4   | Average |
| 1     | 0%                 | 8.2   | 8.1   | 7.8   | 8.0     | 54.8 | 52.7 | 56.8 | 55.7 | 55.0     |
| 2     | 15%                | 10.8  | 10.2  | 10.8  | 10.6    | 68.7 | 69.9 | 71.8 | 68.4 | 69.7     |
| 3     | 20%                | 10.7  | 10.8  | 10.2  | 10.6    | 73.9 | 70.9 | 70.2 | 73.1 | 72.0     |
| 4     | 25%                | 10.0  | 9.4   | 9.7   | 9.7     | 68.1 | 70.4 | 70.6 | 71.0 | 70.0     |
| 5     | 30%                | 9.9   | 9.6   | 10.1  | 9.9     | 68.2 | 70.5 | 69.5 | 70.8 | 69.8     |

It can be seen from Table 3 that compared with the flexural strength of the first set of samples, the flexural strength of the samples containing micro-bead under various dosages is improved, and the increase is between 15% and 20%. The variety of the strength of samples with different dosages of micro-bead is little. The compressive strength of the samples containing micro-bead is significantly improved with a peak appearing in the sample with a content of micro-bead between 15% and 25%.

### 2.7. Comparison of characteristics of different mineral powders

The comparison of the characteristics of grounded blast furnace slag (GBFS), fly ash (FA), SF and micro-bead are shown in Table 4. The micro-bead has the advantages of micro-aggregate filling of SF, and also has strong physical water-reducing and high activity. In the preparation of HPC, not only the water demand is reduced, but also the hydration heat is reduced. Because of its high activity coefficient, the strength of concrete was not reduced after the micro-bead was incorporated. On the contrary, the compactness of concrete was further improved because of its unique micro-aggregate characteristics. Micro-bead provides a new and more effective choice for formulating high performance concrete.

| Characteristics | FA | GBFS | Micro-bead | SF |
|-----------------|----|------|------------|----|
| Main particle size distribution (µm) | 5~30 | 10~40 | 0.1~5 | 0.1~0.5 |
| Grain shape | Mostly spherical | Mostly angular | Completely spherical | Completely spherical |
| Fillability | General | Poor | Good | Good |
| Water reducing | Good | Poor | Excellent | Poor |
| Fluidity | Good | Good | Excellent | Poor |
| Activity | Poor | Good | Good | Good |
| Cracking resistance | Good | General | Excellent | Poor |

### 3. Micro-bead ultra-high performance concrete

In China, HPC with a strength more than 100 MPa is called UHPC. It has been tested and applied in some super high-rise buildings. UHPC with cement, micro-bead and SF compounded as cementitious material is better than that with other ultrafine powders.

#### 3.1. Raw materials

The raw materials used in this study included PII52.5R cement, GBFS with a specific surface area of 8500 cm²/g, micro-bead which was ultrafine FA with a specific surface area of 12540 cm²/g, a loss on ignition of 1.7%, and a water requirement ratio of 92%, SF with a specific surface area of 2×10⁵ cm²/g and a SiO₂ content of 90%, polycarboxylic acid high-efficiency water reducing agent (PA), gravel (G) with the two-stages of 5~9 mm, 9~16 mm being 3:7 and crushing value less than 6%, washed sea sand (SS) with a fineness modulus of 2.8 and mud content less than 0.6%, natural anhydrous anhydrite (NAA)
with a specific surface area of 5200 cm\(^2\)/g and composition of CaSO\(_4\)\(\cdot\)0.022H\(_2\)O, and sulpho-aluminate expansion agent (HCSA).

### 3.2. Mix proportions of concrete

The composition of MUHPC is shown in table 5. In No. 601 concrete, the BASF naphthalene water reducing agent with a solid content of 40% was used. In No. 602, 603, 604, 606 concrete, the naphthalene-ammonia compound water reducing agent (NA) was used. In No. 605 concrete, Sika polycarboxylic acid water reducing agent (SPA) with a solid content of 40% was used.

#### Table 5. Mix proportions of C120 UHPC (kg/m\(^3\)).

| No. | W/B | Cement | Micro-bead | SF | SS | G | Water | Water reducing agent |
|-----|-----|--------|------------|----|----|---|-------|---------------------|
| 601 | 0.20| 500    | 200        | 50 | 750| 1000 | 130   | 22.5                |
| 602 | 0.187| 500    | 170        | 80 | 700| 1000 | 140   | 24.0                |
| 603 | 0.187| 500    | 170        | 80 | 700| 1000 | 140   | 30.0                |
| 604 | 0.187| 500    | 200        | 50 | 700| 1000 | 140   | 26.3                |
| 605 | 0.187| 500    | 200        | 50 | 700| 1000 | 140   | 15.0                |
| 606 | 0.187| 500    | 200        | 50 | 700| 1000 | 140   | 30.0                |

3.3. Performance of fresh concrete

The performance of fresh concrete is shown in table 6.

#### Table 6. Performances of fresh concrete.

| No. | Slump (mm) | Expansion (mm) | Collapse time (s) |
|-----|------------|----------------|-------------------|
|     | Initial    | 1 h | 2 h | 3 h | Initial | 1 h | 2 h | 3 h | Initial | 1 h | 2 h | 3 h |
| 601 | 130        | 680x | 640x | 590x | 540x | 5 | 7 | 9 | 12 |
| 602 | 270        | 260 | 230 | 225 | 700 | 590 | 560 |
| 603 | 260        | 250 | 245 | 255 | 660x | 650x | 670x | 4 | 5 | 7 | 5 |
| 604 | 265        | 710x | 740 | 710 | 690 | 650 | 620 | 670x | 4 | 5 | 5 |

Note: For No. 604 concrete, the 4 h slump is 260 mm, the expansion is 670 mm*730 mm, and the collapse time is 7 s. For No. 602 concrete, the admixture dosage is low (3.2%), and after 3 h, the collapse time is too long which is 12 s. For No. 603 and 604 concrete, the slump, expansion and collapse time are in line with the requirements of this study.

The self-developed sulfamic acid-based water reducing agent is blended with BASF’s naphthalene water-reducing agent (containing 40% solids), and a small amount of zeolite powder mixed with a water-reducing agent can be used to arrange C120 concrete with excellent plasticity. And the C120 concrete can meet long-distance transportation and ultra-high pumping requirements.

### 3.4. Self-shrinkage of concrete
In the mix proportion of C120 concrete, NAA (CaSO₄•0.022H₂O) with a specific surface area of 5200 cm²/g is added. The early age shrinkage of concretes was compared. The mix proportion of concrete is shown in table 7. The performance index of each group of concrete is controlled at: slump of more than 250 mm, slumping extension of 680 mm or more, and collapse time of less than 15 s. Self-shrinkage measurement results are shown in the table 8 and figure 2.

**Table 7. Mix proportions of C120 concrete for self-shrinkage test (kg/m³).**

| Type of concrete                | W/B | Cement | GBFS | Micro-bead | SF | NAA | HCSA | PA | SS | G |
|--------------------------------|-----|--------|------|------------|----|-----|------|----|----|---|
| Reference concrete             | 0.185 | 550    | 42   | 84         | 24 | 0   | 0    |    |    |   |
| Containing 10% anhydrous anhydrite | 0.185 | 550    | 42   | 84         | 24 | 70  | 0    | 4.2% | 750 | 950 |
| Containing 6% HCSA             | 0.185 | 550    | 42   | 84         | 24 | 0   | 42   | 4.2% | 750 | 950 |
| Containing 10% HCSA            | 0.185 | 550    | 42   | 84         | 24 | 0   | 70   | 4.4% | 750 | 950 |

**Table 8. Self-shrinkage of C120 concrete (10⁻⁶).**

| Time | Reference concrete | Containing 10% anhydrous anhydrite | Containing 6% HCSA | Containing 10% HCSA |
|------|-------------------|-----------------------------------|--------------------|---------------------|
| 0 h  | 0                 | 0                                 | 0                  | 0                   |
| 1 h  | 13                | 17                                | 5                  | 30                  |
| 2 h  | 14                | 56                                | 30                 | 124                 |
| 3 h  | 17                | 92                                | 69                 | 162                 |
| 4 h  | 21                | 69                                | 82                 | 142                 |
| 5 h  | 31                | 71                                | 95                 |                      |
| 6 h  | 40                | 181                               | 69                 | 54                  |
| 7 h  | 48                | 196                               | 68                 | 23                  |
| 8 h  | 57                | 204                               | 66                 | 2                   |
| 9 h  | 66                | 210                               | 69                 | -14                 |
| 10 h | 74                | 216                               | 71                 | -26                 |
| 11 h | 81                | 222                               | 73                 | -40                 |
| 12 h | 90                | 226                               | 72                 | -47                 |
| 13 h | 96                | 230                               | 74                 | -55                 |
| 14 h | 103               | 234                               | 74                 | -63                 |
| 15 h | 111               | 237                               | 75                 | -70                 |
| 16 h | 117               | 241                               | 77                 | -76                 |
| 17 h | 124               | 245                               | 79                 | -82                 |
| 18 h | 129               | 244                               | 80                 | -86                 |
| 19 h | 132               | 248                               | 81                 | -89                 |
| 20 h | 139               | 250                               | 83                 | -93                 |
| 21 h | 141               | 253                               | 85                 | -95                 |
| 22 h | 149               | 256                               | 86                 | -98                 |
| 23 h | 150               | 259                               | 88                 | -101                |
| 24 h | 157               | 261                               | 90                 | -103                |
| 2d   | 231               | 312                               | 115                | -116                |
Figure 2. Shrinkage curves of C120 concretes.

It can be seen from table 8 and figure 2 that HCSA can efficiently inhibit the self-shrinkage of concrete. After the incorporation of 5% HCSA into concrete, the 3d self-shrinkage decreased from $269 \times 10^{-6}$ to $138 \times 10^{-6}$, which was reduced by about 50%. After the dosage was increased to 10%, the concrete in 14d was still in a micro-expansion state which was about $90 \times 10^{-6}$. When the HCSA dosage was no more than 5%, the self-shrinkage of UHPC was inhibited. After the incorporation of 10% natural anhydrous anhydrite, the self-shrinkage of concrete in 3d increased from $269 \times 10^{-6}$ to $339 \times 10^{-6}$, which was increased by 26%.

3.5. Compressive strength of hardened concrete
The compressive strength of concrete is shown in table 9.

Table 9. Compressive strength of concrete.

| No. | 3d  | 7d  | 28d | 56d |
|-----|-----|-----|-----|-----|
| 601 | 85.8| 97.5| 130 | 140 |
| 602 | 87.1| 102 | 135 | 145 |
| 603 | 84.3| 102 | 140 | 150 |
| 604 | 75.1| 96  | 120 | 130 |

4. Influence of fiber on the mechanical properties of MUHPC
The fiber was blended into the original C120 concrete to improve the mechanical properties. The mix proportions of polypropylene fiber were 1.0 kg/m$^3$ and 2.0 kg/m$^3$, respectively. And the mix proportion of the organic fiber of Shenzhen was 2.0 kg/m$^3$.

4.1. Pole body compressive strength and static elastic modulus
The static compression modulus test is shown in figure 3.
The static compression modulus test results are shown in Table 10. It can be seen from Table 10 that after the fiber is incorporated, the compressive strength of the prism is low, but the static elastic modulus is high.

**Table 10. Prismatic compressive strength and static compressive modulus of concrete.**

| No. | Age (d) | Size of sample (mm) | Prismatic compressive strength | Static compressive modulus |
|-----|---------|---------------------|-------------------------------|-----------------------------|
|     |         |                     | Individual | Average | Individual | Average |
| Reference | 28     | 100×100×300        | 115.2      | 138.0    | 5.20×10⁴   | 5.20×10⁴ |
|         |         |                     | 138.0      |          | 5.18×10⁴   |          |
|         |         |                     | 138.8      |          | 5.22×10⁴   |          |
| Fiber 1 kg | 28     | 100×100×300        | 127.2      | 128.7    | 5.10×10⁴   | 5.23×10⁴ |
|         |         |                     | 126.8      |          | 5.21×10⁴   |          |
|         |         |                     | 132.0      |          | 5.37×10⁴   |          |
| Fiber 2 kg | 28     | 100×100×300        | 137.2      | 136.6    | 5.22×10⁴   | 5.30×10⁴ |
|         |         |                     | 139.0      |          | 5.22×10⁴   |          |
|         |         |                     | 133.6      |          | 5.45×10⁴   |          |
| Fiber 2 kg | 28     | 100×100×300        | 104.8      | 116.7    | 5.18×10⁴   | 5.25×10⁴ |
| Shenzhen |         |                     | 116.4      |          | 5.23×10⁴   |          |
|         |         |                     | 128.8      |          | 5.33×10⁴   |          |

4.2. Fracture toughness test of concrete

The fracture parameter test of C120 concrete is shown in figure 4.

The load-crack opening displacement (P-CMOD) curves of four groups of concrete with reference, fiber 1 kg, fiber 2 kg and fiber 2 kg (Shenzhen) were determined. And the corresponding fracture parameter values, including cracking strength, tensile strength, bending strength, fracture energy and brittleness parameters were calculated. There were three test pieces for each concrete. Figures 5-8 show the P-CMOD curves of each group of concrete and the calculated concrete softening relationship (σ-w) curve.
Figure 4. Fracture parameter test of C120 ultra-high performance concrete. (a) Closed-loop hydraulic servo test machine and (b) Placement of the deformation sensor.

Figure 5. P-CMOD curve and σ-w curve of reference concrete. (a) P-CMOD and (b) σ-w.

Figure 6. P-CMOD curve and σ-w curve of concrete with 1 kg fiber. (a) P-CMOD and (b) σ-w.
Figure 7. P-CMOD curve and σ-w curve of concrete with 2 kg fiber. (a) P-CMOD and (b) σ-w.

Figure 8. P-CMOD curve and σ-w curve of concrete with 2 kg fiber (Shenzhen). (a) P-CMOD and (b) σ-w.

It can be seen from figures 5-8 that the P-CMOD curve and the σ-w curve are similar in shape between different test pieces of the same kind of concrete, and the difference is not large, indicating that the dispersion between the test pieces is not big.

According the complete P-CMOD curve, its corresponding fracture parameters can be calculated. Table 11 shows the fracture parameter values of different types of concrete. It can be seen from table 11 that the cracking loads of different types of concrete are basically the same. This is because the matrix material is the same, and the fiber is mainly used after the concrete is cracked. As the fiber content increases, the tensile strength of the concrete is substantially unchanged, and the fracture energy of the concrete increases. When the same amount is used and the fiber types are different, the concrete fracture energy is also different. The magnitude of the fracture energy is based on the reference <fiber 1 kg < fiber 2 kg (Shenzhen) < fiber 2 kg. The brittle characteristic length is a physical quantity characterizing the degree of brittleness of concrete. The brittleness of the concrete increases when the characteristic length of concrete decreases. According to the test results, it can be seen that as the fiber content increases, the toughness of the concrete increases. The length of the brittle characteristic length is based on the benchmark <fiber 1 kg < fiber 2 kg (Shenzhen) < fiber 2 kg, and the corresponding concrete toughness is based on the benchmark < fiber 1 kg < fiber 2 kg (Shenzhen) < fiber 2 kg.
5. Durability of concrete
The Cl– diffusion coefficient and freeze-thaw resistance of C120 concrete were tested.

5.1. Cl– diffusion coefficient
For the reference concrete, the concrete prepared by river sand (RS), and the concrete prepared by washed SS, the chloride ion diffusion was tested by the NEL method established by Tsinghua University. The test results are shown in Table 12. According to the durability design and construction standard evaluation of concrete structure [7], the permeability grade is IV and the permeability is very low.

Table 12. Results of Cl– diffusion coefficient of C120 UHPC.

| No. | Sample type | Age (d) | Cl– diffusion coefficient (m²/s) | Test basis |
|-----|-------------|---------|---------------------------------|------------|
| 1   | Reference   | 28      | 0.62×10⁻¹²                      | NEL method for rapid detection of chloride ion diffusion coefficient in concrete |
| 2   | RS          | 28      | 0.57×10⁻¹²                      |            |
| 3   | SS          | 28      | 0.64×10⁻¹²                      |            |

5.2. Frost resistance test
According to the standard requirements [8], C120 concrete was subjected to 300 freeze-thaw cycles. The results are shown in Table 13.

Table 13. Results of frost resistance of C120 UHPC.

| Content                             | Result | Standard requirement |
|-------------------------------------|--------|----------------------|
| Relative dynamic elastic modulus after | 99.9   | When the concrete is freezed and thawed to a |
### 110 freeze-thaw cycles (%)

| Mass loss rate after 110 freeze-thaw cycles (%) | predetermined number of cycles, and the relative dynamic elastic modulus is not less than 60%, or the mass loss rate is not more than 5%, it can be considered that the frost resistance of tested concrete has met the design requirements. |

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### 6. Conclusion

Through the detection of micro-bead performance, the preparation and detection of MUHPC, the durability test and the detection of the mechanical properties of MUHPC with the incorporation of fiber, the conclusions of the research work are as follows:

- **Micro-bead** is an ultrafine powder of spherical glass body with a maximum particle size of 1.45 μm and a minimum particle size of 2.38 nm. The cement–micro-bead–silica powders can be combined in appropriate proportions to make the porosity of the powder to reach the minimum. And the concrete has the highest fluidity under the same water consumption, or the water demand is the lowest under the same fluidity.

- **UHPC** with the cement–micro-bead–silica powder as the main binder and incorporated with the appropriate water reducer has a strength reaching up to 150 MPa and a plasticity reaching up to 3 h (the initial slump being 265 mm–265 mm, expansion being 710 mm×740 mm–670 mm×710 mm, the collapse time being 4 s–5 s) and no bleeding segregation phenomenon.

- On the basis of the reference C120 UHPC, with the incorporation of 5% sulfo-aluminate bulking agent, the self-shrinkage is reduced from 269×10⁻⁶ to 138×10⁻⁶, which is reduced by about 50%. And when a small amount of sulfo-aluminate salt expansion agent is added, the self-shrinkage cracking of UHPC can be effectively inhibited.

- The C120 UHPC has a low Cl⁻ diffusion coefficient and is resistant to freeze-thaw damage and has a high durability.

- For the C120 UHPC incorporating polypropylene fiber with contents of 1 kg/m³ and 2 kg/m³, the shape of the load-crack opening displacement curve (P-CMOD) or the softening relationship curve (σ-w) are nearly the same, and the cracking load is basically the same. This is because the base material of the concrete is the same, and the fiber can play a role mainly after the concrete is cracked. As the fiber content increases, the fracture energy, the brittle characteristic length and the toughness of the concrete all increase.

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