Study on the effect of fly ash and polycarboxylic acid water reducer on the properties of recycled concrete

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Abstract: By testing the compressive strength, tensile strength, permeability coefficient, carbonization depth and relative dynamic elastic modulus, the influence of fly ash and polycarboxylic acid superplasticizer on the performance of recycled concrete was studied. The mechanism of action of fly ash and polycarboxylic acid superplasticizer on concrete properties was also analyzed by SEM. The results indicate that the compressive strength, tensile strength, permeability coefficient relative and dynamic elastic modulus of recycled concrete are increased by 7.1%, 8.3%, 81.0% and 16.7% respectively, the carbonization depth decreased by 34.4%, when the cementitious materials is replaced by 20% (by mass) of fly ash and 1.2% (by mass) of polycarboxylic acid superplasticizer. Therefore, fly ash and polycarboxylic acid superplasticizer can effectively promote the hydration of cement particles and improve the pore structure of concrete along with the bond between cement paste and recycled aggregate in the interface transition zone, which is suitable for the preparation of high performance recycled concrete.

1. Introduction
With the development of industrialization and cities, the world's demand for aggregate and cement used in concrete is increasing every year, which may lead to the scarcity of natural resources in the
future. For one thing, it is estimated that by 2020, China's construction waste production will reach a peak of 2.6 billion tons, a large amount of demolished construction waste has caused landfill problems. For another thing, fly ash is a by-product of coal-fired power plants, the treatment of fly ash also brings environmental problems.

An important option to reduce environmental problems is to replace natural aggregates with recycled aggregates and cement with auxiliary cementitious materials such as fly ash [1-10], because the amount of demand for natural aggregate and cement construction is increasing. In addition, in terms of technology and environment, it is not enough to study the simultaneous incorporation of these alternative materials and traditional components [11-15], there is also a lack of literature review on mixed fly ash and high content recycled coarse aggregate concrete.

In addition, the use of recycled concrete aggregate instead of natural aggregate will reduce the mechanical properties of recycled concrete. However, the concrete strength of replacing at least 30% of the natural aggregate with recycled aggregate will not endanger the safety of the structure [1]. The durability related performance of concrete is also affected by the recycled aggregate [16]. On the other hand, fly ash increases the long-term strength of concrete, especially in the case of low incorporation amount, reducing the required water content [14,15]. In terms of durability, fly ash improves the durability characteristics of most concrete [17,18]. These trends have prompted researchers to mix the two materials for greener concrete with acceptable mechanical and durability.

For this reason, the regenerated aggregate was modified with double admixture of fly ash and polycarboxylic acid, improve the recycled aggregate and cement paste of the cohesive force of interface transition zone, make up the gap between layer, improve the mechanical properties, deformation performance, durability properties and microscopic properties of recycled concrete, in order to provide reference for modification research and engineering application of recycled concrete.

2. Material and test methods

2.1. Material

P·O 42.5 Portland cement was used as the main cementitious material in recycled concrete. Class C fly ash was used as a part of cementitious materials in recycled concrete. The chemical composition of these cementitious materials are listed in Table 1.

The nature river sand was used as fine aggregate with a fine modulus of 2.6. The natural coarse aggregate is made of limestone gravel with a grain size of 5 ~ 40mm. The strength grade of C40 waste concrete was broken and screened, and the coarse aggregate with a particle size of 5-40mm was formed. The properties of coarse aggregate are shown in table 2. The polycarboxylate-based superplasticizer with water reduction rate of 33.8% was used.

| Raw Materials | Chemical compositions (%) |
|---------------|---------------------------|
| Cement        | CaO 65.52, SiO₂ 22.45, Al₂O₃ 4.49, Fe₂O₃ 4.13, MgO 1.47, L.O.I 1.00, SO₃ 0.94 |
| Fly ash       | CaO 3.23, SiO₂ 54.26, Al₂O₃ 26.37, Fe₂O₃ 12.56, MgO 0.74, L.O.I 0.86, SO₃ 0.49 |

| Table 2. Performances of coarse aggregates. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Species         | Density (g/cm³) | Bulk density (g/cm³) | Water absorption rate (%) | Mud content (%) | Crushing value (%) |
| Natural aggregates | 2.70            | 1.45             | 0.59             | 0.60             | 9.6               |
| Recycled aggregates | 2.60            | 1.36             | 2.81             | 1.59             | 14.2              |
2.2. Mixture proportioning
For the test study, the concrete with strength grade C30 was selected. The mixing ratio of ordinary concrete was $m(\text{cement}) : m(\text{water}) : m(\text{sand}) : m(\text{stone}) = 309:170:741:1208$.

Double mixing fly ash and poly carboxylic acid water reducing agent of proportion of recycled concrete for $m(\text{cement}) : m(\text{fly ash}) : m(\text{water}) : m(\text{sand}) : m(\text{renewable}) : m(\text{water reducing agent}) = 280, 280, 152:703, 152, 4.8$.

2.3. Compressive strength test
The compressive strength test pieces were cubes (150 x 150 mm in size, and curing at the temperature of 15-25°C and the relative humidity of 95-100% for 7d, 14d, 28d, 56d, 90d. Continuous and uniform loading at the speed of (0.3-0.5)MPa•s$^{-1}$ was applied to the failure, the failure load was recorded and the compressive strength was calculated.

2.4. Tensile strength test
The tensile strength test pieces were cubes (150 x 150 mm in size, and curing at the temperature of 15-25°C and the relative humidity of 95-100% for 7d, 14d, 28d, 56d, 90d. Continuous and uniform loading at the speed of (0.04-0.06)MPa•s$^{-1}$ was applied to the failure, the failure load was recorded and the tensile strength of concrete was calculated.

2.5. Modulus of elasticity test
The size of the specimens using phi (150×300) mm, and curing at the temperature of 15-25°C and the relative humidity of 95-100% for 7d, 14d, 28d, 56d, 90d. Continuous and uniform loading at the speed of (0.2-0.3)MPa•s$^{-1}$ was applied to the failure, the failure load was recorded and the elastic modulus of concrete was calculated.

2.6. Permeability coefficient test
The specimen with top diameter of 175 mm, the mouth diameter of 185 mm, 150 mm high frustum of a cone, standard curing to 28d, comes out in 0.8 MPa to 1.2 MPa stand for 24 h under constant pressure, measuring water penetration height, concrete relative permeability coefficient was calculated.

2.7. Carbonation depth test
The specimen were cubes (150 x 150 mm in size, after standard curing to 28d. Then remove the specimen to the temperature of 15-25°C, the concentration of CO$_2$ from 17% to 23% and the relative humidity of 65%-65% to carbonation for 7d, 14d, 28d, the average carbonation depth were calculated.

2.8. Relative dynamic modulus of elasticity test
The specimen size in 100mm×100mm×400 mm prism, standard curing to 28d, then Freezing-thawing cycle 50, 100, 150, 200 times, the averag relative dynamic elastic modulus and the mass loss rate were calculated.

2.9. Porosity test
Porosity measurements were carried out with QUANTACHROME Pore-master GT-60. Samples were taken from the broken specimen after compression test and were oven-dried at 65 °C for 24 hours.

2.10. Scanning electron microscopy (SEM)
When the concrete reaches the corresponding age, the hydration is terminated with absolute ethanol, and the concrete is broken into fragments. The samples are dried to constant weight at 60°C. The samples are pasted on the copper sample base by conductive adhesive. After vacuum, the effect of water reducer and fly ash on the micro-morphology of concrete is observed by scanning electron microscope.

3. Results and discussion

3.1. Analysis of aggregate performance
Compared with natural limestone aggregate, the apparent density of recycled aggregate decreased by 3.7%, the bulk density decreased by 6.2%, the water absorption rate increased by 376%, the mud content increased by 165%, and the crushing value increased by 47.9%.

3.2. Compressive strength and tensile strength of recycled concrete
As shown in figures (Fig. 2) and (Fig. 3), the test results show that the compressive strength and tensile strength increased with the increase of age for recycled concrete that mixed with fly ash and polycarboxylic acid water reducer. Compared with normal concrete, the compressive strength of recycled concrete mixed with fly ash and poly carboxylic acid water reducer decreased by 3.9% and 0.6% respectively after 7 and 14 days, but compressive strength increased by 7.1%, 8.6% and 7.2% respectively after 28, 56 and 90 days. The tensile strength decreased by 4.5% after 7 days, but the tensile strength increased by 4.3%, 8.3%, 7.7% and 7.1% respectively after 14, 28, 56 and 90 days. The reason is that firstly the cement mortar attached to the surface of the recycled aggregate adds additional cement particles, which increases the cement content of the recycled concrete. The additional cement particles contain a large amount of Ca(OH)₂, which can help fly ash particles absorb CaO and generate C-S-H, the main contributor to strength development. Secondly, as shown in table 1, the content of SiO₂ in fly ash particles reaches at 54.26%, and high percentage of SiO₂ also will cause Ca(OH)₂ reacts in early stage. Therefore, when high content of recycled aggregate and fly ash is added, the fly ash particles exceeding the standard limit can be used as an ash binder rather than a filler. Furthermore, poly carboxylic acid water reducer can effectively promote the cement hydration at early stage, reduce the plastic shrinkage caused by ettringite transformation in later stage. So the improvement effect is more apparent in later stage and can significantly improve the hydration products microstructure, Ca(OH)₂ is refined and the distribution more even, the porosity is reduced and the cement stone structure is more compacted.
3.3. Elastic modulus of recycled concrete

Figure (Fig. 4) shows, test results show that the elastic modulus increased with the increase of age for recycled concrete mixed with fly ash and polycarboxylic acid water reducer. Compared with ordinary concrete, the elastic modulus of recycled concrete with fly ash and polycarboxylic acid water reducer decreased by 4.3%, 3.6%, 4.5%, 2.6% and 2.3% respectively after 7d, 14d, 28d, 56d and 90d. The effect of fly ash and polycarboxylic acid water reducer on the elastic modulus of recycled concrete is not as great as that of recycled aggregate. This is because the elastic modulus depends on the composition of concrete. The properties of aggregate, cement slurry, age and permeability are the most important factors affecting the elastic deformation of concrete. The elastic modulus of recycled aggregate is lower than natural aggregate is because that the content of adhesive mortar in recycled aggregate is lower than that of natural aggregate. Therefore, the elastic modulus of recycled concrete is opposite to the compressive and tensile strength.

3.4. Impermeability of recycled concrete

As shown in table (Tab. 3), the test results show that with the adding of fly ash and poly carboxylic acid water reducer, the permeability of concrete is improved greatly. Compared with ordinary concrete, water penetration height for fly ash and poly carboxylic acid water reducer mixed concrete fell by 68.4%, the permeability coefficient was reduced by 81.0%, this may related to fly ash’s particle accumulation and pozzolanic effect in concrete. Fly ash and polycarboxylic superplasticizer can increase the fluidity of concrete, so less water is needed to maintain the workability of equivalent
ordinary concrete. Compared with cement slurry, the slurry mixed with fly ash and polycarboxylic acid water reducer is denser. Therefore, the recycled concrete mixed with fly ash and polycarboxylic acid water reducer shows higher anti-penetrability performance.

Table 3. Impermeable abilities of Concrete.

| Species            | Seepage height /mm | Relative seepage height /% | Permeability coefficient /cm/h |
|--------------------|---------------------|-----------------------------|-------------------------------|
| Ordinary concrete  | 95.7                | 63.8                        | 6.42 x 10^-6                  |
| Recycled concrete  | 30.2                | 20.1                        | 1.22 x 10^-6                  |

3.5. Carbonization resistance of recycled concrete

The test results in table (Tab. 4) show that the carbonation depth of the concrete with the mixture of fly ash and polycarboxylic acid water reducer decreased by 39.0%, 30.5%, 20.8% and 34.4% respectively in 3d, 7d, 14d and 28d. This is mainly because in the concrete mixed with fly ash and polycarboxylic acid water reducing agent can enhance the capacity of long-term the carbonation resistance of recycled concrete. The reasons for this behavior is because in the big time, hydration will produce in the fly ash in concrete, and coarse pore volume and the total porosity is due to the produce of secondary C-S-H is reduced, the carbonization rate decreased. In this way, the anti-carbonization ability of the regenerated concrete is improved by mixing fly ash and polycarboxylic acid water-reducing agent.

Table 4. Test results of carbonation performances of concrete.

| Species            | Carbonization depth /mm |
|--------------------|--------------------------|
|                    | 3 d | 7 d | 14 d | 28 d |
| Ordinary concrete  | 4.1 | 5.9 | 7.2  | 9.3  |
| Recycled concrete  | 2.5 | 4.1 | 5.7  | 6.1  |

3.6. Frost resistance of recycled concrete

According to SL352-2006, when the reduction of dynamic elastic modulus is less than 40% and the mass loss of concrete is less than 5%, concrete is considered to be anti-freeze. Figure (Fig. 5) shows the relative dynamic elastic modulus and mass loss rate of concrete after 200 freeze-thaw cycles. First, the relative dynamic elastic modulus of concrete and the mass loss rate proportional to the number of freeze-thaw cycle, two kinds of concrete antifreeze performance meet the requirement of SL352-2006, and second, compared with ordinary concrete, double blending polycarboxylic acid water reducing agent and fly ash concrete in 50, 100, 150, after 200 times of freeze-thaw cycle, relative dynamic elastic modulus increased by 5.6%, 5.9%, 11.8% and 5.9% respectively, the mass loss was reduced by 50.0%, 54.5%, 52.4% and 50.0% respectively. Compared with the type of aggregate, the reduction of water-cement ratio, the addition of fly ash and polycarboxylic acid water reducer have greater influence on the frost resistance of recycled concrete.
3.7. Recycled concrete micropore structure
At the same time, the pore structure of hardened mortar in regenerated concrete with ordinary concrete and double-doped fly ash and polycarboxylic acid water-reducing agent was analyzed, as shown in table 5. The pore diameter classification in table (Tab. 5) is based on the theory of literature [19], that is, less than 50nm is harmless hole, [50,100]nm is less harmful hole, and more than 100nm is harmful hole. From the pore size distribution: by adding polycarboxylic acid water reducing agent, in the concrete introduced a large number of tiny air bubbles is less than 200 microns, compared with normal concrete, recycled concrete double mixing fly ash and polycarboxylic acid water reducing agent and the harmful pore ratio is greatly reduced, the proportion of harmless hole greatly improve, so the concrete permeability resistance, carbonation resistance and freeze resistance performance has improved obviously.

Table 5. Pore distribution of mortar in hardened concrete.

| Species          | Aperture distribution /% | Air-void spacing factor/μm |
|------------------|--------------------------|----------------------------|
|                  | < 50 nm                  | [50,100] nm                | > 100 nm                   |
| Ordinary concrete| 43.6                     | 37.2                       | 19.2                       | 388                        |
| Recycled concrete| 55.8                     | 35.7                       | 8.5                        | 236                        |

3.8. Scanning electron microscopy (SEM)
By scanning electron microscopy (SEM) observation we found that polycarboxylic acid water reducer can effectively promote the cement hydration at early stage, accelerate the calcium sulfur acid salt and aluminate hydration, prompting early transformation of ettringite Aft to single type sulfur sulphur aluminate Afm to reduce the ettringite plastic shrinkage in later transformation. The improvement effect is more apparent in later stage and can significantly improve the hydration products microstructure, Ca(OH)₂ is refined and the distribution more even, the porosity is reduced and the cement stone structure is more compacted, as shown in Figure Fig. 6.

Secondly, the non-uniform matrix and spherical particles of fly ash can still be seen 90 days later (Fig. 7). This indicates that the ash reaction of fly ash mixed concrete is slower than that of ordinary concrete. The interfacial transition zone of recycled concrete mixed with fly ash and polycarboxylic acid water reducer is superior to that of ordinary concrete (Fig. 8). This is because the recycled aggregate absorbs large quantity of water and plays the role of internal curing since a large number of
Recycled cement particles contains Ca(OH)$_2$ and fly ash also contains high amounts of SiO$_2$. So, through the combination of water, Ca(OH)$_2$ and SiO$_2$, C-S-H increases and fills the ITZ area, and effectively improves the interface bonding between the recycled aggregate and cement.

(a) Hydration of 7-day morphology of antonym hydrated with PolycarboxylateSuperplasticizer  
(b) Hydration of 28-day morphology of antonym hydrated with PolycarboxylateSuperplasticizer  
Figure 6. Morphology of hydration products of concrete mixed with PolycarboxylateSuperplasticizer.

(a) FA blending level is 0%  
(b) FA blending volume by 30%  
Figure 7. Microstructure of cement matrix after hydration for 90 days.

(a) Interfacial transition zone between cement and paste aggrecommon gates  
(b) the Interfacial transition zone between fly ash slurries and recycled aggregates  
Figure 8. Morphology of hydration products with fly ash concrete.

4. conclusion

Compared with natural limestone aggregate, the apparent density and accumulation density of reclaimed aggregate decreased, while the water absorption, mud content and crushing value of reclaimed aggregate were higher than that of natural aggregate.
Recycled concrete double mixing fly ash and poly carboxylic acid water reducing agent, compared with ordinary concrete, the 28 d compressive strength increased by 7.1%, the tensile strength increased by 8.3%, 4.5% lower elastic modulus and permeability coefficient reduced by 81.0%, 34.4% lower carbonation depth and relative dynamic elastic modulus increased by 16.7%, the mass loss rate by 43.8%.

The adsorption and dispersion of polycarboxylic acid water reducer not only improved the fluidity of the slurry, but also promoted the early transformation of Af to Afn of monosulfur-type thioaluminate and the hydration of cement particles. Micro aggregate effect, morphological effect of fly ash, ash effect complement each other, make all kinds of effect is more apparent, double mixing fly ash and poly carboxylic acid water reducing agent can improve the recycled concrete mechanical properties, deformation properties and durability.

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