Effect of fly ash on mechanics and microstructure of alkali-activated recycled cement

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Abstract. The effect of fly ash on mechanical performance of alkali-activated recycled cement was studied. The result shows that the cement types have a significant impact on the strength of alkali-activated recycled cement pastes. The alkali-activated recycled cement pastes prepared from fly ash cement (PF) have higher strength. When replaced by 15%~30% of fly ash, the strengths of alkali-activated recycled cement pastes prepared from ordinary Portland cement and slag cement can be significantly improved. When the replacement of fly ash added to 15%, the 90 days flexural and compressive strengths of the alkali-activated recycled PS cement pastes were 6.2 MPa and 30.9 MPa. Image (SEM) of the alkali-activated recycled PS cement pastes replaced by 15% fly ash showed that the microstructure is more uniform and compact than that unmodified.

1. Introduction
According to a report by the Chinese Academy of Sciences, about 2.4 billion tons of construction waste is produced in China every year [1], and it takes for over 40% of the total urban garbage. Researchers [2-4] have made extensive use of these waste concrete as recycled aggregate concrete, however, it has a few disadvantages such as low strength, greater water demand and high porosity, which restricts its widely applications. A few researchers [5-9] put forward that waste concrete powders as a cement admixture or concrete composite owned hydrability and grindability, and only its replacement ratio stays low enough that the mixed cement can accord with strength requirement. Moreover, Fang [10-12] suggested that it is possible to active the activation of recycle mortar powder by alkali activators and produce a new kind of cementitious materials. However, the workability and mechanics performance of alkali-activated recycled cement can not satisfy application requirements. Efforts should be contributed to advance the strength and performance through morphological effect, active effect and micro-aggregate effect. The present work studied the effect of fly ash on mechanics and microstructure of alkali-activated recycled cement.

2. Materials and methods

2.1. Raw materials
P·II 42.5, P·S 42.5 and P·F 42.5 cements from Jiangnan-Onoda Cement Corporation in Nanjing were used for preparing the imitation recycled cements. Fly ash, which accords Chinese standards, was utilized as a mineral admixture. Water glass with the SiO₂/Na₂O modulus of 1.4 was used as the
activator, the dosage of water glass was 5% by weight of the dried cement paste.

2.2. Methods
Hardened cement pastes prepared from different cement types were cured in a steam curing box of 99 ℃ for 30 days, then cracked and dried at 200 ℃ for 2 h, and recycled cement powders were ground by mill until the specific area up to 380 m²kg⁻¹. Recycled cement powders were prepared from different cement types of P·II 42.5, P·S 42.5 and P·F 42.5, which simulated the waste concrete powders, named as PII, PS and PF respectively. The recycled cement powders activated by 5% water glass with w/c of 0.5 was formed to the paste specimens of 20×20×80 mm, then cured at standard curing room of 20 ± 2 ℃, above RH > 90% for 90 days. If the content of fly ash reaches to 15%, the alkali-activated recycled cement pastes prepared from P·II 42.5 were named as PIIA15. The compressive and flexural strengths with different aged were obtained using the electronic universal testing machine. The images of hardened pastes with the 28 day aged were captured using a Hitachi SU8010 scanning electron microscope (SEM) 20kv.

3. Results
3.1. Effect of cement types to mechanics
Figure 1 shows the mechanics of the recycled cement pastes prepared from different cement types. Three kinds of cement (PII, PS and PF) pastes appear poor mechanical properties, and PF activated by water glass has the best performance of strength development, where the compressive strength of pastes was 24.3 MPa at 90d, and the flexural strength was 5.3 MPa at 90d. In general, the recycled cement powders contain hydrates, unhydrated cement, unreacted mineral admixtures and so on. Owning to long ages of cement hydration, unhydrated cement clinker has lower content. Forming new reconstructive hydrates in hardened pastes were responsible to the strength development. Moreover, the great difference of three type cement pastes is the content of fly ash and slag. Therefore, unreacted active mineral admixture plays an important role in the alkali-activated reaction system. There was none unreacted active mineral admixture in the recycled cement powders of PII, and the cement pastes prepared from PII have the lowest compressive and flexural strengths. Since the high activity of slag, the degree of hydration reaction is higher and the residual content of active SiO₂ and Al₂O₃ in PS is less than in PF. To summarize, the alkali-activated recycled cement hardened pastes prepared from PF indicates the best performance of the three.

![Figure 1](image)

Figure 1. Mechanics of the recycled cement pastes prepared from different cement types

3.2. Effect of fly ash content to mechanics
As the replacement ratio of fly ash increase, the alkali-activated recycled cement pastes has better performance of molding effects and strength development in PII and PS than in PF. Figure 2 shows the mechanics of the alkali-activated recycled cement pastes replaced by 0, 15% and 30% fly ash
respectively were tested at 3, 28- and 90-day ages. When the replacement rate of fly ash added to 15%, the compressive strengths of the hardened pastes, prepared from PII and PS, increased by about 40%~100%. With the increasing of the replacement rate of fly ash from 15% to 30%, the slower growth in strength would appear. On the contrary, it indicated that the mechanical property of the recycled cement pastes decreased obviously with the increase of fly ash content. The experimental results show that the 3, 28, and 90-day compressive strengths of PS pastes replaced by 15% fly ash reached 17.6 MPa, 27.4 MPa and 30.9 MPa, and the flexural strengths reached 2.2 MPa, 4.4 MPa and 6.2 MPa, respectively. Simultaneously, with curing period increasing, long age strength was growing faster than early age strength. The reason might be that fly ash became gelation slowly along with the reaction. The compressive strength was first increased and then decreased along with the increasing of fly ash content. Numerical results indicate that there is an optimum dosage of fly ash ranging from 15%~30%.

Figure 2. Mechanics of the recycled cement pastes with fly ash replacement

3.3. Microstructures

Compared with the hardened pastes (Figure 3(a)) prepared from PS at 28d aged, the hardened pastes prepared from PS with 15% fly ash replacement (Figure 3(b)) expressed totally different microstructure: In the hardened pastes prepared from PS, there were a lot of relatively deep pores appeared on newly formed and original hydrates with granular or spherical adsorption, which is dispersively distributed around the hardened cement structure. Therefore, it can be inferred that the pastes activated by water glass shows a layer structure, it is composed mainly of newly formed gel-like hydrates. But some strips can be observed between new and old pastes boundary connection.

In the hardened pastes replaced by 15% fly ash at 28d aged, these new hydration products can not only fill in pores but it also formed C-S-H gels with network structure and C-A-H gels with layers structure. under the effect of OH\(^{-}\) from the dissolution of water glass, [\(\text{SiO}_2\)]\(^4\) and [\(\text{AlO}_2\)]\(^5\) ions which were released from the broken Si-O-Si bonds and Si-O-Al bonds were dissolved into the aqueous phase and promoted the original C-S-H gels, C-A-H gels and Ca(OH)\(_2\) to form newly hydrates. In the medium stage of hydration, alkali solution with high PH gradually packaged and destroyed the silicon oxygen network structures, then a large number of [\(\text{SiO}_4\)]\(^4\) and [\(\text{AlO}_4\)]\(^5\) ions incorporated with calcium to form hydrated gels filling the early age hydrates. It is mainly because of the low ratio of CaO/SiO\(_2\) and CaO/Al\(_2\)O\(_3\), these gel-like hydrates \([13-14]\) designated as (N, C)-A-S-H gels with large specific surface are covered with Na\(^+\) ions which resulted in lower alkalinity. Further reason that the proper proportion of CaO-SiO\(_2\)-Al\(_2\)O\(_3\), it can constitute a kind of new and renewable cementitious material owned more compact microstructure.
4. Conclusion

All studies show that the cement types have a significant impact on the mechanics of alkali-activated recycled cement pastes. When the alkali-activated recycled cement pastes were prepared from fly ash cement (PF), the hardened pastes have the highest strength. Meanwhile, as an activity admixture for recycled cement powder, fly ash has an obviously enhancement effect on PII and PS. And there is an optimum dosage of fly ash ranging from 15%~30%. After 90 days curing cycle, the compressive and flexural strength reached approximately 6.2 MPa and 30.9 MPa, respectively, and the hardened pastes has a more compact microstructure and better mechanical property.

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