論 文 の 内 容 の 要 旨

論文題目　　Development of ultra-high strength zero-cement mortar
（超高強度ゼロセメントモルタルの開発）

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Concrete is the most consumed material next to water in the world. In the production of Portland cement, which is the main component of concrete, there are some negative environmental impacts such as increased CO_2 emissions, large consumption of raw materials and energy, and emission of harmful environmental pollutants. In general, firing 1 ton cement clinker will generate 1 ton CO_2. So far, mixing Portland cement with industrial waste such as ground granulated blast-furnace slag powder and fly ash has greatly contributed to CO_2 reduction. However, further reductions in CO_2 emissions are required under the Paris Agreement, which came into effect in November 2016. In recent years, alkali activated materials, which uses waste by-products that can significantly reduce CO_2 emissions during manufacturing compared to Portland cement, is attracting attention from around the world as a CO_2 reduction measure.

For easier understanding and differentiation, the alkali activated materials are divided into two categories: one type uses NaOH and Na_2SiO_3 with high alkalinity as alkali activator, which is called high alkali activated zero-cement, and another type uses CaO with low alkalinity as alkali activator, which is called low alkali activated zero-cement.

The aim of this thesis is to develop an ultra-high strength zero-cement mortar of more than 100 MPa and to elucidate of the influencing factors and mechanism of ultra-high strength zero-cement mortar, and to propose the design method for ultra-high-strength zero-cement mortar in order to reduce CO_2 emissions and provide theoretical basis and technical support for practical application.

In the first, study the development of high alkali activated zero-cement mortar. For the compressive strength, how much influence do various factors have? Is it relevant? And can it make zero-cement? In order to confirm that, first, as a preliminary experiment, according to the

Taguchi Method, it was confirmed that it could have a different effects in the presence of various factors. Then, innovatively measured the gel content of high alkali activated zero-cement, and elucidate mechanism of ultra-high strength high alkali activated zero-cement by clarifying the relationship between the pore structure, reaction products and compressive strength. In this experiment, the alkaline solution was prepared by mixing NS and NH (12mol/L) at a mass ratio of 2: 1, the mass ratio of the alkaline solution to the powder is 0.5. The mass ratio of FA to BF was five levels of 100: 0, 75:25, 50:50, 25:75 and 0: 100. At 7 days, the compressive strength tended to increase as the replacement rate of ground granulated blast furnace slag increased. The 7 days compressive strength of the specimen BF100 was 86 MPa. At 28 days, the specimen FA25BF75 showed the highest strength instead of the specimen BF100, and its compressive strength was 104 MPa.

The total pore volume tended to decrease as the replacement rate of ground granulated blast furnace slag increased. Compared with 7 days, the total pore volume of all the specimens showed a tendency to decrease at 28 days. Unlike cement mortar, the compressive strength of high alkali activated zero-cement mortar showed a low correlation with the pore volume of more than 50 nm, and it may be related to the formation of different hardened matrix. Specimen FA75BF25 and FA50BF50 had the higher gel content, but not lead to higher strength. The compressive strength of alkali-activated materials is not simply determined by the gel content. The type of gel also has a huge effect on the strength. It can be considered that the contribution of higher Ca/Si ratio gels to strength is greater.

Compressive strength have a linear relationship with the weight loss ratio (W) (105℃-300℃) (R^2=0.8792). From the overall trend, the greater the weight loss ratio (105℃-300℃), the greater the compressive strength. However, some points deviate from the linear relationship. In order to evaluate the compressive strength more accurately, a new index needs to be proposed. The strength index and strength have a high correlation (R^2=0.9533). It is effective to use the strength index to evaluate the compressive strength of the zero-cement mortar.

Secondly, the development of low alkali activated zero-cement mortar were also studied. In preliminary experiment, compared low alkali and high alkali activated zero-cement, which demonstrate that the use of a low alkaline activator can also develop a high strength zero-cement mortar. The specimens 1-2 (SF: FA: BF = 1.5: 2.5: 6) compressive strength at 3 days increase to 35 MPa and the compressive strength at 28 days reach up to 95 MPa.

For the effects of alkali activators content and curing condition, at 20℃ curing, the more the low alkali activator content used, the greater the compressive strength at 7 and 28 days. The maximum strength at 7 days is 70.2 MPa, and the maximum strength at 28 days is 79.8 MPa. At 90℃ heat curing, as the content of low-alkali activator increases, the compressive strength increases first and then decreases. When the low-alkali activator content is 80 kg/m^3, the maximum compressive strength in 7 days reach up to 136 MPa.

For the effects of active CaO-Al_2O_3-SiO_2 content, the higher the content of RCaO and RAl_2O_3, the greater the 7days compressive strength. The higher the RCaO content, the greater the 28days compressive strength. The change of Young's modulus is consistent with the change of compressive strength. The higher the Young's modulus, the higher the compressive strength. Compressive strength has a correlation with saturated water content. The lower the saturated water content, the greater the compressive strength. The XRD analysis shows that the main reaction product of low alkali zero-cement is composed of a glass phase (gel) indicated by a halo peak of 18 to 35°(2θ) and a crystal phase of Hemicarbonate ($C_4Ac_{0.5}H_{12}$), Straetlingite (C_2ASH_8) and Portlandite ($Ca(OH)_2$). As the content of RCaO increases, the amount of Straetlingite produced gradually decreases. Regardless of the $RSiO_2/RAl_2O_3$ molar ratio, when the RCaO content is low, low-alkali activated zero-cement tends to form Straetlingite. From the overall trend, the greater the weight loss ratio (105℃-300℃), the greater the compressive strength. When $RSiO_2/RAl_2O_3$ is same, the compressive strength and strength index have a high liner correlation (R^2 is 0.9749, 0.9799 and 0.9894). At the same strength index, the smaller the $RSiO_2/RAl_2O_3$ ratio, the greater the compressive strength, indicating that the generated CASH gel with lower $RSiO_2/RAl_2O_3$ ratio contributes more to the strength. It is possible to use the strength index to evaluate the compressive strength. The compressive strength can be predicted by the weight loss ratio (105℃-300℃) and the percentage of saturated water content.

For the effects of water/binder ratio, the bigger the binder/water ratio, the greater the compressive strength, and it showed an approximate linear function correlation. The strength is determined by the combined effect of the degree of pozzolanic reaction and the distance between the particles.

For the effects of particle size, the finer the particle size of BF, the higher the compressive strength of the mortar at early age. Higher fineness BF and higher specific surface area can increase the speed of pozzolanic reaction. However, the compressive strength of some BF4000 samples even exceed BF8000 samples at later age. The difference in compressive strength between the type II SR group and the type III SR group is very small, the type I SR group with the largest specific surface area has the highest compressive strength.

For the effects of type of raw materials, Regardless of W/B=45% or W/G=45%, when the amount of SR or FA used is small, the compressive strength of the SR group and the FA group is very close. However, when the content of SR or FA increase, the compressive strength of the FA group is smaller than that of the SR group due to different dissolution rate. In the later age, the gap between the compressive strength of the FA group and the SR group gradually decreased.

Thirdly, the design methods for ultra-high strength zero-cement mortar are proposed. Compared to the ACI model, the zero-cement model can predict the compressive strength of zero-cement mortar more accurately. For zero-cement, a value and b value have a high linear correlation. a value is dependent on the zero-cement's RCaO, RAl_2O_3 and $RSiO_2$ content. It can approximately represent the reaction rate of zero-cement binder. The larger a value, the slower the reaction rate. the value of a have the highest correlation with S/(C+A) molar ratio. With the increase of S/(C+A) molar ratio, a value also increases. Therefore, as long as the percentage of RCaO, $RSiO_2$ and RAl_2O_3 contained in zero-cement is determined, the strength development of zero-cement mortar can be predicted; the prediction model can expresses a value, in the form of a function of age, glass content/water ratio. It is considered useful as an estimation equation for strength development of zero-cement mortar. When different types or different particle sizes of raw material are used, a and b always satisfy the linear correlation.

It is also possible to predict the strength development of zero-cement simply by C/(S+A) molar ratio. Regardless of high-alkali activation or low-alkali activation, the relative compressive strength of 7 days and 28 days has a high correlation with C/(S+A). From the overall trend, the greater the C/(S+A), the higher the relative compressive strength. When the molar ratio exceeds 0.9, the increase in relative compressive strength gradually stabilizes.

Finally, the CO_2 emissions based on 1 m^3 of zero-cement mortar mix were quantified. The CO_2 emissions generated by 100MPa mortar comprising zero-cement binders and OPC based binder were compared. The CO_2 emissions of $1m^3$ low alkali activated zero-cement mortar was approximately 57.4% less than $1m^3$ OPC based mortar. For high alkali activated zero-cement mortar, the CO_2 emissions value is highly related to the proportions of sodium silicate and sodium hydroxide used in the mix proportion of mortar, which can be largely varied. Compared with $1m^3$ cement based mortar, the CO_2 emissions of $1m^3$ high alkali activated zero-cement mortar increased by 6.2% and decreased by 17% and 6.8%, respectively.

The present work studied essential factors which have considerable effect on the compressive strength of zero-cement. At the same time, the mechanism of ultra-high-strength zero-cement mortar was also studied. Besides, a design method for ultra-high strength zero-cement mortar was proposed as well. But there are still many problems to be further studied, such as effect of dissolution rate of raw materials, effects of the type of gel produced on the strength contribution rate, strength diagram of quaternary components considering the influence of Na and effects of trace elements.