Experimental Investigation on imitative RPC Material to Sulphate Attack

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Abstract
An imitative RPC material was acquired, based on the idea of porosity reduction of set material by optimizing the granular size distribution of dry blend. Regularly the blend was composed of cement, fine crushed aggregate, sand and silica fume, and characterized by high silica fume content, a certain of rubber powder and very low water to binder ratio. The binder used was formatted by silica fume, ultra-pulverized fly ash, and ordinary Portland cement. Local natural medium crude sand in I / II grading zone and a crushed limestone fine aggregate with the size range from five to ten mm were also applied here. Rubber powder with fifty meshes was added to replace part of sand for agreeable flexibility. Properties of various reference concrete series were investigated by conducting multiple tests, including the permeability test, the mechanical strength test, the salt solution absorption test, the accelerated sulphate attack test, and etc. The imitative RPC material was proven to be environmental-friendly by the test results, and exhibits favorable mechanical strength, high impermeability, and excellent durability to sulphate attack.
Keywords: IMITATIVE RPC MATERIAL, SALT SOLUTION ABSORPTION TEST, RESISTANCE TO SULPHATE ATTACK, ENVIRONMENT-FRIENDLY MATERIAL, TUNNEL LINING CONCRETE

1. Introduction

High durability materials are put forward for various scenarios on concrete durability. In 1990s, a French man named Richard. P from Bouygues Company acquired a new concrete material by imitating the DSP materials[1, 2], and its main content was active powders, naming the Reactive Powder Concrete (abbre. RPC) [3, 4]. Invention of RPC threw a silver lining on the durability of concrete and entitled it a broad foreground in practical application. RPC materials have extensive application in producing various incredibly strong prefabrications with high durability [5] and the world's first pedestrian/bicycle bridge was built with RPC 200 materials [6]. RPC materials is pricey because the coarse aggregates were removed and replaced with quartz sands, along with less water but high contents of active powders were applied [2-4]. This paper investigates the properties to sulphate attack of mortar series with various cement-based binders to select the electee for binder. According to the principle of RPC, an imitative RPC material (abbre. imit-RPC, the same as below) was acquired with the local natural medium crude sand, fine crushed limestone, a compounded binder of ordinary Portland cement, high content of silica fume and certain content of fly ash, and etc. Properties of the concrete series against sulphate attack were investigated, by employing an accelerated method of unilateral-leaching with high concentrated sodium sulphate solution. Indexes like compressive strength, chloride ion permeability and sulphate salt solution absorption were measured for engineering needs.

2. Experimental program

2.1. Materials and Specimens

Four concrete series were selected to be references in this study and represent varieties. They were individually standing for the ordinary concrete, the ultra-pulverized fly ash concrete, the polymer concrete and the high-performance concrete. The samples use local natural medium crude sand in I / II grading zone. The aggregate are crushed limestone with the size range from five to ten mm. Silica fume with a specific surface area of 20,470 m^2/kg and an ultra-pulverized fly ash with a specific surface area of 800 m^2/kg bought from Xiangtan power plant were used. Rubber powder with 30~50 meshes grinding from waste tire are added to relieve strain. Table 1 summarizes the concrete mixture components in this investigation. Those ingredients were mixed, stirred by a forcible mixer, and then cured in saturated limewater solution at 20±2°C after demolded. Specimens with a size of 100mm×100mm×100mm were prepared for compressive strength test. Some others of 150mm×150mm×150mm were cored and cut in a size of ø100mm×50 mm for measuring penetrability. Cylinder specimens with a size of ø100 mm×150 mm were prepared, and the specimens were drilled with a power drill fitted with 50mm diameter water flush diamond tipped barrels. The cavity of the specimens were blocked, sealed at the bottom with epoxy resin, and then filled with sulphate solution. The core cylinders were prepared for salt absorption tests. The selected experimental solution is 50,000/150,000 ppm sodium sulphate solution which is prepared by mixing pure sodium sulphate into distilled hot water and sit at 25°C for twenty four hours.

2.2. Testing procedures

Compressive strength was measured at seven days age according to Standard GB/T 50081-2002. Permeability of chlorine ion was measured according to ASTM C 1202 method. Tolerance against sulphate attack was designed with accelerated method. Specimens were undergoing unilateral-immersion into fifteen percent sodium sulphate solution at seven days age and stored in the creep room with a temperature at 20±2°C and relative humidity at fifty to sixty percent.

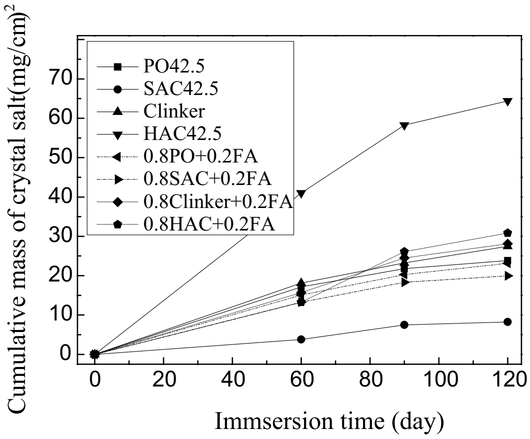
3. Results and Discussion

3.1. Summary of the composition optimization for binder

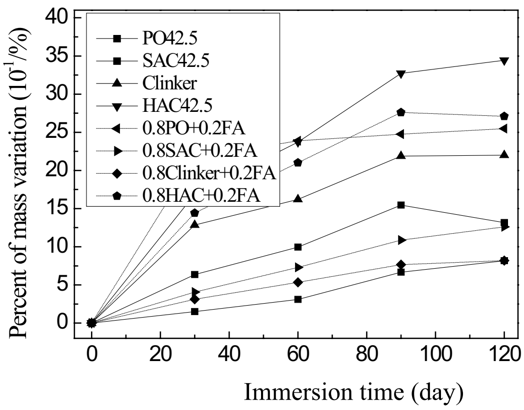
In order to acquire a qualified candidate binder for imit-RPC materials, a conducted composition optimization for cement-based materials was adopted to withstand sulphate attack. Two reference mortar series were prepared with w/b=0.4, and made of Portland cement (abbrev. P.O. 42.5), ground cement clinker, sulphoaluminate cement (abbrev. SAC 42.5), and aluminous cement (abbrev. HAC 42.5), respectively. One was an ordinary mortar serial; the other was a mortar serial added with silica-aluminum materials. The mortar specimens had been cured in a saturated limewater solution to seven days after demolded, and then immigrated into 50,000 ppm sodium sulphate for semi-immersion. The cumulative mass of crystal salt and the total mass (crystal salt and the prism) variation were measured with a same interval (described in Fig.1). The results showed that the mortar with HAC. 42.5 accumulated the maximum mass of crystal salt, and the general order was HAC 42.5> P.O. 42.5>clinker> SAC 42.5. When silica-aluminum materials replace part of cements, the cumulative mass of crystal salt decreased in all series, and the order of salt crystallization was HAC 42.5> SAC 42.5> P.O. 42.5> clinker. In Fig.1 (b), the Portland ordinary cement serial with silica-aluminum materials exhibited a high ratio of increase in total mass during the first thirty days, and then moved to a slow increasing stage. The clinker serial and SAC 42.5 serial in control group have small increase on the total mass while both the reference group while the fiducial group of with HAC 42.5 have high increasing ratio. It was supposed to be caused by the abundant calcium hydroxide produced by clinker serial and the P. O. 42.5 serial, and stimulated the pozzolanic activity of silica-aluminum materials. The C-S-H of second pozzolanic reaction refined the capillary and densified the matrix. For SAC 42.5 serial and HAC 42.5 serial, the replacement of

Table 1. Detail components of the concrete mixtures (mass ratio, dimension less)

Concrete serial	P.O 42.5	SAC42.5	SF	FA slag	Polymers	Rubber powder	Sand	Aggregate	Water	Super-plasticizer
1	100	/	/	/	/	/	200	200	40	0.4
2	/	100	/	/	/	/	200	200	40	0.4
1-1	75	/	5	20	/	/	200	200	40	0.3
1-1A	75	/	3	20	2	/	200	200	40	0.3
Imit-RPC	70	/	15	10	/	5	100	100	18.6	1.2



(a) Cumulative mass of crystal salt



(b) Total mass variation

Figure 1. Properties of salt crystallization and total mass variation

cement by silica-aluminum materials enlarged the w/c ratio and complicated the simulation of pozzolanic activity [7]. In summary, Compound of Portland ordinary cement and the silica-aluminum materials was an electee binder for imit-RPC materials.

3.2. Compressive strength of concrete series

Fig.2 shows the seven days compressive strength of the reference concrete series at seven days age. It can be seen that the strength of RPC serial was three times of the normal concrete. Strength grades of the other three concrete series were equivalent. Compressive strength of the polymer-modified concrete serial was relatively higher than that of the other two series due to the redisperable polymer powder blocking and refining the porous [8, 9]. The seven days compressive strength of additional salic-mineral serial scored lowest due to the replacement of silicon-aluminum material for equal cement enlarged w/b and the pozzolanic activation of salic-mineral at the early age. Strength of the sulphoaluminate cement serial is slightly higher than the normal concrete serial for its main ingredient of clinker is a typical high early strength mineral. The high-grade strength of imit-RPC serial mainly originated from several aspects. Firstly, the hydrates were densified because of the low ratio of water to binder and the optimized granular size distribution of the dry blended binder. Secondly, the formation of C–S–H by the reaction between silica fume with CH was activated. The secondary hydrate reaction consumed the bulk wafer CH to form low C/Si ratio C-S-H gels [9, 10].

3.3. Penetration and absorption of concrete series

Fig.3 and Fig.4 are the permeability and absorption test results of concrete series at seven-day age, respectively. The index of penetration was expressed as the electric flux within six hours. Seen from Fig.3, penetrability of imit-RPC was extremely low. The electric flux was 21.2 coulombs, accounting for only 0.7% of the ordinary concrete serial. Though the electric flux was slightly below, the sulphoaluminate concrete serial has an equivalent permeability grade to that of ordinary concrete serial. The ultra-pulverized fly ash concrete serial exhibited equivalent permeability with the polymer-modified concrete serial. The replacement of silica fume with polymers suppressed the content of salic mineral. Polymer blocked the capillary porosity that would weaken the pozzolanic

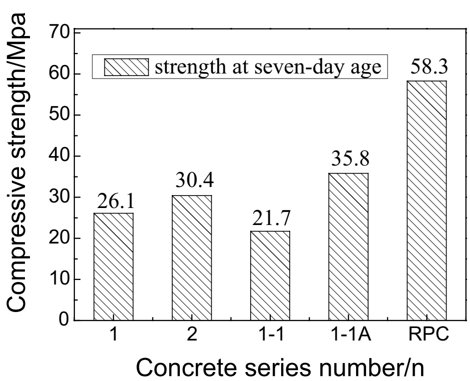


Figure 2. Compressive strength of various mortar series

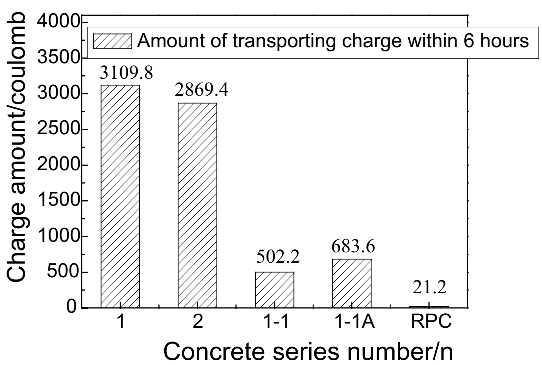


Figure 3. Poperties of chlorine penetratiorn

reaction, and that was why penetrability of the polymer-modified concrete serial was slightly higher than the ultra-pulverized fly ash concrete serial. Result of salt absorption solution collaborated well with the result of penetration tests. Implied by Fig.4, the amount of salt solution absorption increased sharply in the first several hours and slowed down gradually. When the absorption equilibrium was reached, it suspended the absorption according to the outside environment. The total salt solution absorption ranked as following, ordinary concrete serial> the ultra-pulverized fly ash concrete serial> the polymer-modified concrete serial > the imitative RPC serial. The time needed for equilibrium ranked as imit-RPC serial < the polymer-modified concrete serial < the ultra-pulverized fly ash concrete serial < the sulphoaluminate ordinary concrete serial< the Portland ordinary concrete serial.

3.4. Resistance of various concrete series to sulphate attack

Semi- immersion test were conducted at seven days age. Specimens were exposed to 50,000 ppm sodium sulphate solution after saturated mass was weighted by an electronic weighing system. Index of total mass variation was monitored at an interval of thirty days. Property to sulphate attack was evaluated by total mass variation. Fig.5 is the total mass variation of various concrete series after semi-immersed in 50,000 ppm sodium sulphate solution. The total mass variation of the imitative RPC serial was the least in

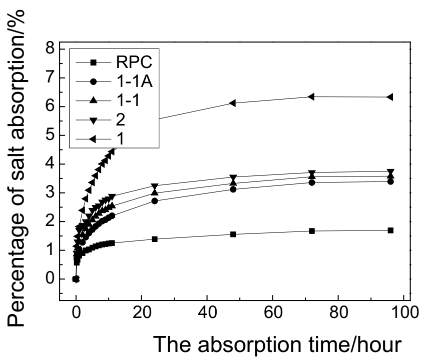


Figure 4. Properties of absorbing salt solution

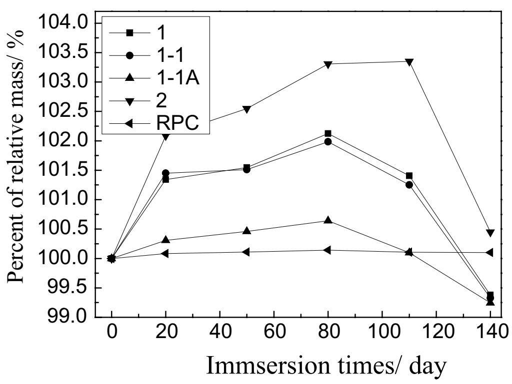


Figure 5. Total mass variation of concrete serial

all reference groups. The general ranking is that the imit-RPC serial < the polymer-modified concrete serial < the ultra-pulverized fly ash concrete serial < the Portland ordinary concrete serial < the sulphoaluminate ordinary concrete serial. Except the imitative RPC serial, the ultra-pulverized fly ash concrete serial and the two ordinary concrete serials exhibited significant mass variation. The total mass increased by 2.0% after eighty days of immersion, and decreased to approximately 99.3% by one hundred and forty days. The mass of the polymer-modified concrete serial increased rather slightly at first stage and then dropped to the point similar to ordinary concrete serial, by one hundred and forty days. Those conclusions kept identical with the results of penetration test and salt solution absorption test.

In order to simulate the sulphate attack on tunnel lining concrete, three selected concrete series were subject to unilateral-leaching in sodium sulphate solution. The unilateral-leaching test was conducted with following procedures. Firstly, selected specimens were excavated by a power drill and sealed its bottom by epoxy resin. Then, the treated cubes were covered with a piece of glass after its inner cavity filled with 150,000 ppm sodium sulphate solution. Afterwards, the prepared specimens were stored in environment with the temperature at 20±2°C and relative humidity at 0.5~0.6. Fig.6 shows the salt crystal and appearance disintegration after the concrete specimens unilateral-leaching in sodium sulphate solutions. It can be seen that some well growth deterioration occurred to the three reference ordinary concrete serials for salt crystallized in the upper zone of the four mould surface. From the Fig. 6 (a) &Fig.6 (b), it can be seen visible salt crystals and its spalls the capillary adsorption zone around leaks of the Portland ordinary concrete specimens after one hundred and twenty days of unilateral leaching age. When the crystallized salt was removed, it can be seen that the geometric dimension and quantity of capillary is increased greatly. The ultra-pulverized fly ash concrete serial and the polymer-modified concrete serial demonstrated better performance in salt crystallization than the Portland ordinary concrete serial. The sulphoaluminate ordinary concrete serial has the worst deterioration while the imit-RPC exhibits excellent resistance to sulphate attack. Salt crystals were spotted on surface of the sulphoaluminate ordinary concrete cube. The surface layer of concrete was cracking, spalling and then flaking off the matrix after seventy days of unilateral immersion. The concrete of imit-RPC retained its geometric integrality. The surface of concrete was clean, nothing but a little salt crystallized on the mould surface for the one hundred days of immersion time.

(a)P.O=1.0, w/c=0.4 (b) P.O=1.0, w/c=0.4 (salt removed) (c) SAC=1.0, w/c=0.4

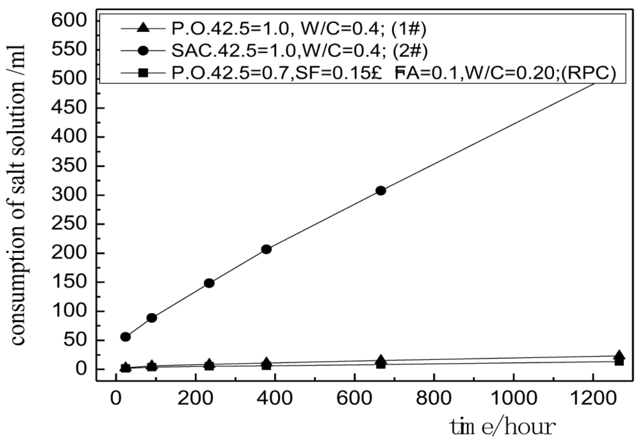
(d)P.O=0.75, FA=0.20, SF=0.05 (e) P.O=0.75, FA=0.20, SF=0.03, Poly=0.02 (f) imitative RPC

Figure 6. Unilateral leaching in 150,000 ppm sodium sulphate solution

Fig. 7 shows the concrete unilateral immersed in fifteen percent sodium sulphate solution. The consumption of salt solution is monitored by a graduated glass tube connected with the cavity of concrete cylinder. Solution consumption of concrete serial named the Portland ordinary concrete serial (1#), the sulphoaluminate ordinary concrete serial (2#) and the imitative reactive powder concrete serial (imit-RPC) was presented. It can be seen that the salt solution consumption of sulphoaluminate ordinary concrete serial is far larger than that of the Portland ordinary concrete serial and the imit-RPC serial. The solution consumption between the Portland ordinary concrete serial and the imit-RPC serial is equivalent, and the

(a) Panorama of the unilateral leaching test

(b) Typical photos of concrete deterioration



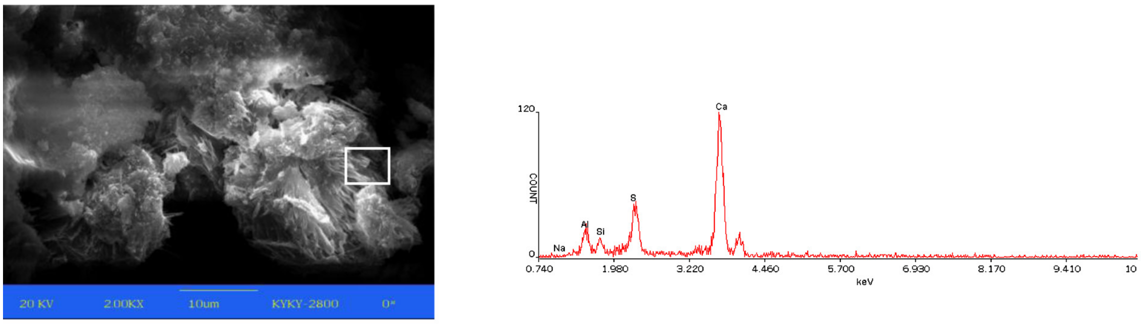
(c) Sodium sulphate solution consumption of concrete serials

Figure 7. Unilateral leaching test

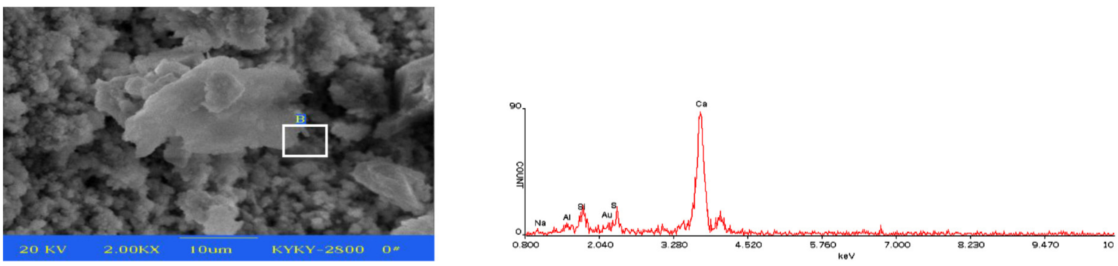
Portland ordinary concrete serial have slightly more consumption of the sodium sulphate solution. The result unilateral immersion test and consumption of sodium sulphate solution identifies a second time that the imit-RPC serial has high-performance to sulphate attack.

3.5. Microstructure of concrete

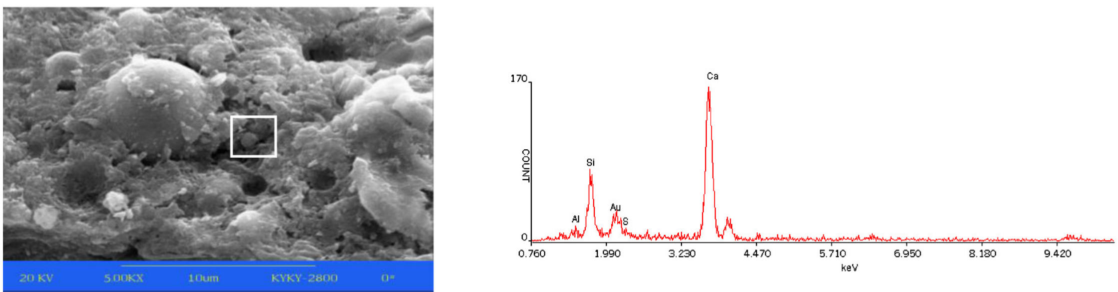
SEM image and energy spectrum expound excellent performance of the imitative RPC materials to sulphate attack. Images and energy diagrams selected from the Portland ordinary concrete (denoted by 1#), the mineral admixed concrete (denoted by 1-1a#) and the imitative RPC materials (denoted by RPC#) were shown in Fig.8. It can be seen that the microstructure of Portland ordinary concrete differed obviously from that of mineral admixed concrete and the imitative RPC materials. Seen from the image of 1# concrete, there is many erosion products due to the reaction between hydration calcium aluminum, portlandite and sodium sulphate. The flaky ettringite and calcium sulphate gathered into clustered mass. These hydration products and sodium sulphate from environmental solution for leaching separated from aperture solution produced a large expanding force in concrete and, therefore, resulted in the severe degradation of properties. In image of 1-1a# / 1-1#, there are only hydration products of C-S-H, portlandite and the fly ash fine pellets can be seen. The hydration gels and fine fly ash granules packed so densely that no growing space was left for ettringite and gypsum development. In SEM image of the imitative RPC sample, the fly ash pellets were buried or wrapped by plenty of hydrate/ secondary C-S-H gels. The secondary C-S-H deposited in the pores thereby made concrete close-grained and impermeable [11], and therefore, blocked the penetration paths for sulphate ions through the concrete matrix [12]. For mixture with extreme low water to cement, addition of fly ash and high content of silica fume contributes greatly to the excellent performance to sulphate attack by greatly decreased the porosity, especially the capillary of concrete. Such great changes then effectively hindered the rapid transportation of sulphate ions and the consumptions of portlandite, restrained the production of ettringite and calcium sulphate [13].



(a) Serial 1# concrete



(b) Serial 1-1# &1-1a# concrete



(c) Serial imitative RPC materials

Figure 8. SEM images and EDS spectrum of various serials

4. Conclusions

The imitative RPC material displayed excellent retrofit potentials on mechanical strengthening, high impermeability and excellent durability to sulphate attack.

Compared to conventional RPC, the introduction of fine aggregate and the rubber powder contents reduced size shrinkage when enhanced flexibility. The imitative RPC material possessed economic and engineering benefits.

The stable and compact geometrical interior structure-liked contents of hydration gels hindered the rapid transportation of ions in sodium sulphate solution and, therefore, endowed the imitative RPC materials with qualified performance in sulphate environment.

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