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Mechanical Properties and ITZ Microstructure of Recycled Aggregate Concrete Using Carbonated Recycled Coarse Aggregate

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Abstract: The effect of carbonation treatment and mixing method on the mechanical properties and interfacial transition zone (ITZ) properties of recycled aggregate concrete (RAC) was investigated. Properties of recycled concrete aggregate (RCA) were tested firstly. Then, five types of concretes were made and slump of fresh concrete was measured immediately after mixing. Compressive strength and splitting tensile strength of hardened concrete were measured at 28 d. Meanwhile, the microstructure of RAC was analyzed by backscattered electron (BSE) image. It was found that the water absorption ratio of carbonated recycled concrete aggregate (CRCA) was much lower when compared to the untreated RCA. Comparatively, the apparent density of CRCA was not significantly modified. The concrete strength results indicate that the mix CRAC-2 prepared with CRCA by adopting two-stage mixing approach shows the highest compressive strength value compared to the other mixes. The microstructural analysis demonstrate that the mix CRAC-2 has a much denser old ITZ than the untreated RAC because of the chemical reaction between CO_2 and the hydration products of RCA. This study confirms that the ITZ microstructure of RAC can be efficiently modified by carbonation treatment of RCA and encourages broadening the application of construction and demolition wastes.

Key words: recycled aggregate concrete; compressive strength; interfacial transition zone; carbonation treatment; two-stage mixing approach; back scattered electron

1 Introduction

In the fields of concrete production, substitution of natural aggregate with recycled aggregate generated from construction and demolition wastes (CD&W) is receiving ever growing attentions because it can not only conserve natural resource but also mitigate the adverse environmental effect, thus facilitating the sustainable development of concrete industry. However, the mechanical properties and durability of recycled aggregate concrete (RAC) have been found to be inferior to that of conventional concrete as a result of poor physical properties of recycled concrete aggregate (RCA), for example, high water adsorption and low density[1,2].

Different methods were reported to improve the quality of RCA by removing or strengthening the attached mortar[3-5]. Carbonation treatment of RCA was suggested to be one of the promising ways to enhance the quality of RCA because of the low cost and utilization of CO_2[6]. Kou *et al*[7] reported that the water sorption of recycled mortar aggregate (RMA) decreased by the use of CO_2 curing and the properties of RAC made with RMA were improved. Zhang *et al*[8] attempted to improve the quality of RCAs through carbonation of attached cement paste and showed that carbonation could improve the density and decrease the water sorption and crushed value of RCAs. The extent of CO_2 curing of the recycled aggregate was quantified and the influencing factors referring to carbonation process such as curing time, particle size and moisture contents of the recycled aggregates were studied[9]. Furthermore, the properties of mortar made with carbonated RCA have also been experimentally

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investigated; The results showed that water absorption, dry shrinkage and chloride migration of mortar got reduced when compared to the control sample[10]. Nevertheless, there are few studies focusing on the ITZ of RAC. Carbonation in cement-based products can be defined as a reaction between the CO_2 dissolved in water and the cement hydration product such as $Ca(OH)_2$ in the pore water. This reaction produces calcium carbonate and water. Calcium silicate hydrates and calcium aluminate hydrates can also react with CO_2 to produce calcium carbonate, hydrates of silicates and aluminates[11].

The aim of this study is to investigate the effect of carbonation treatment of RCA and mixing method on the mechanical properties and microstructure of RAC. Thermogravimetric analysis (TGA) was applied to evaluate the performance of carbonation treatment. Workability of fresh concrete, compressive strength and splitting tensile strength of hardened concrete were measured and compared to that of controll concrete. Scanning electron microscopy was typically used to investigate the microstructure of RAC. Findings from this study provide useful information for enhancing the performance of RAC in order to encourage and broaden the application of construction and demolition wastes.

2 Experimental

2.1 Materials

Cement CEM I 42.5N, natural aggregate (NA), recycled concrete aggregates (RCA) were used in this study. RCAs were obtained from a local recycling plant in Lausanne, Switzerland. The compressive strength of original waste concrete was unknown. The size of RCAs used in this study ranged from 5-16 mm.

2.2 Carbonation treatment of RCA

RCAs were put in a glove box connected with a commercially available carbon dioxide bottle (concentration of CO_2, 100%) and the concentration of CO_2 in the box could be monitored; The relative humidity (RD) of atmospheres in the box was adjusted by putting a small box of $Mg(NO_3)_2$ which can help achieve a balanced RD about 60%, which facilitates the proceeding of the carbonation process. An electrical fan was also employed in the box to accelerate the circulation of CO_2. The duration of carbonation process was 3 weeks continuously.

2.3 Mix proportion

Five types of concrete mixtures were cast in laboratory, including natural aggregate concrete (NAC) as reference concrete. Normal mixing approach (NMA) and two stage mixing approach[12] (TSMA) were used in this study. It was reported that TSMA can improve the compressive strength of RAC by filling some pores and cracks of RCA. Different from NMA, TSMA divides the mixing process into two parts and proportionally splits the required water into two which are added at different time. For convenience, RACs were marked with CRAC-1, CRAC-2, URAC-1 and URAC-2. For example, CRAC-1 represents that the RCA was produced with CRCA using NMA; URAC-2 represents that the RCA was produced with untreated RCA using modified TSMA. Based on the sieve analysis of NA and RCA, a comparable particle size distribution curve was achieved. The concrete mixes formulation is shown in Table 1, with the same effective ratio of water to cement (w/c=0.40).

Table 1 Mix proportion of concrete

Mixture	Material content/(kg/m^3)				Mixing method
	Cement	Water	NA	RCA	
NAC	487	203	1 687	0	NMA
CRAC-1	487	226	1 179	505	NMA
CRAC-2	487	226	1 179	505	TSMA
URAC-1	487	234	1 177	506	NMA
URAC-2	487	234	1 177	506	TSMA

The mixing and casting of all types concrete mixtures were done at 20 ℃. The total required water consisted of free water and additional water absorbed by RCA, but only half of the total required water was mixed with aggregates first and the rest part of the total required water was added following cements. The duration between the two stages when the water was added was extended to 10 mins so that the RCA can absorb more water to improve the workability of RAC. All samples in this experiment were cylinders, with the dimension of ϕ110×220 mm. After 24 h, the samples were demoded and cured in a standard curing chamber.

2.4 Test method

Physical properties: Water absorption and apparent density of aggregate were measured according to GB14685-2011[13].

Mechanical strength: Compressive strength and splitting tensile strength were determined on 3 cylinder samples at 28 d; test was conducted carefully at a loading rate of 0.5 MPa/s according to GB50081-2009.

Micro-analysis: TGA-Thermogravimetric analyses were carried out with a Mettler Toledo TGA/SDTA 851 balance to evaluate the carbonation treatment of RCA. Samples powders were collected by carefully scraping the old attached mortar in RCAs and the whole process was conducted in a vacuumed glove box, avoiding further carbonation in atmosphere (concentration of CO_2, 0.03%). 20 mg of sample was further crushed into a finer powder and heated at a constant rate of 10 ℃ /min from 30 to 950 ℃ in a 10 mL/min flow of nitrogen. Related information can be found in Ref.[14].

BSE-For image analysis, the slices were stopped hydration first and then impregnated under vacuum with epoxy resin. After 24 h, the impregnated slices were polished carefully from 9 to 1 um using diamond sprays. The polished samples had been carbon coated before they were examined by backscattered electron (BSE) image in a scanning electron microscope (SEM, FEI Quanta 200) with an accelerating voltage of 15 kV and magnification times of 2 000. More detailed information about SEM sample preparation could be found in Ref.[15].

3 Results and discussion

3.1 Water absorption, apparent density and thermogravimetric analysis of RCA

Water absorption and apparent density of natural aggregate (NA), un-carbonated RCA (URCA) and carbonated RCA (CRCA) were measured. From Table 2, it can be seen that URCA showed much higher water absorption (6.53%), which is about 10 times that of NA. It was interesting to note that water absorption of CRCA was dramatically decreased, only 5.12%, which means that a reduction of up to 21.6% was achieved. This is in consistent with the reported results[8,10]. The results demonstrated that carbonation treatment can improve the quality of RCA by reducing the water absorption of RCA, which can be attributed to the reactions of carbon dioxide with the hydration products of old mortar. However, the apparent densities of all aggregates were very close in this experiment, about 2 700 kg/m^3.

Table 2 Main physical properties of aggregates

Type of aggregate	24 h Water absorption/%	Apparent density /(kg/m^3)
NA	0.65	2 690
CRCA	5.12	2 670
URCA	6.53	2 660

During carbonation process, CO_2 can react with main hydration products such as calcium hydroxide (CH) and hydrated calcium silicate (C-S-H). Consequently, a higher amount of $CaCO_3$ will be formed in the old mortar. It was widely accepted that carbonated calcium decomposes at around 400 ℃, leading to a mass loss in sample. Therefore, the content of $CaCO_3$ can be calculated by the mass loss at around 400 ℃ due to CO_2 emission. Fig.1 shows that the content of $CaCO_3$ in adhered mortar of CRCA is around 51%, which is much higher than that of URCA. This can be attributed to the carbonation treatment on RCA. The results further confirm that the simple apparatus for carbonation treatment is very effective to modify the quality of attached mortar of RCA.

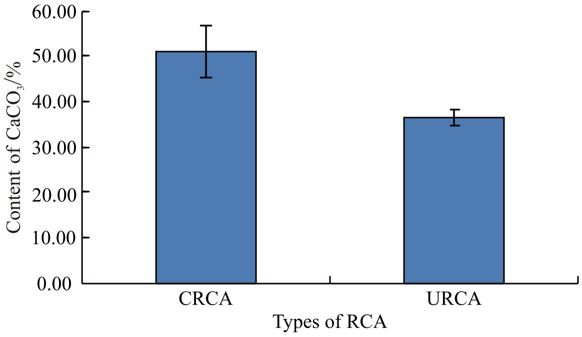

Fig. 1 Comparison on the content of $CaCO_3$ in old adhered mortar of different RCAs

3.2 Workability of fresh concrete

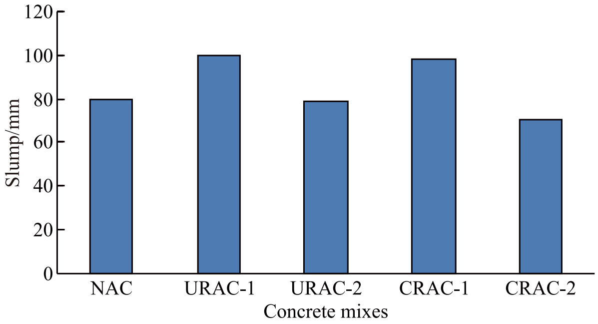

Fig.2 Slump value of different concrete mixes

Taking high water absorption of RCA into consideration, we added 90% of water absorbed by RCA used in the mix to reach the same effective water to cement ratio. Slump test of fresh concrete was carried out immediately after mixing. As shown in Fig.2, the slump value of NAC was 80 mm which is considered to be the target slump value in mix design. Both URAC-1 and CRAC-1 which were fabricated using NMA have a higher slump value about 100 mm, whereas URAC-2 and CRAC-2 have a lower slump value. This is due to the fact that the water was divided into two parts and separately added in the mixer in TSMA, which signifies that the RCAs have sufficient time to absorb water leading to the formation of a thin layer of cement slurry on the surface of RCA and leaving less free water in the fresh mixture. It should be noted that although no super-plasticizer has been added to the concrete mixes, four types of RACs show satisfied workability in comparison with NAC.

3.3 Mechanical properties of hardened concrete

3.3.1 Compressive strength

The compressive strength of all concrete mixtures is shown in Fig.3. It is observed that four RAC mixtures have a slightly higher compressive strength value than that of the reference mix NAC. Furthermore, it is evident that the CRAC-2 which was prepared with carbonated RCA by adopting two-stage mixing approach shows the highest compressive strength value (28 d) compared to the other mixes.

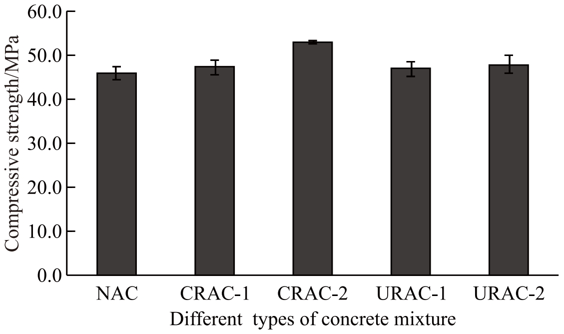

Fig.3 Comparison on 28 d compressive strength among different concrete mixtures

It can also be found that the compressive strength of URAC-2 is a little bit higher than that of the mix URAC-1, which indicates that TSMA does have a positive effect on the compressive strength development of RAC. The results compare well with previous studies[16,17]. This is due to the fact that the first half amount of water can facilitate the formation of thin cement slurry on the surface of RCAs which will permeate into the porous old cement mortar, filling up the old cracks and voids[18].

By comparing the strength results of CRAC-2 and URAC-2 which were made using RCA with and without carbonation treatment, the former mixture gained much more in compressive strength development. The results are consistent with other research results[10, 19]. This demonstrates that carbonation treatment of RCA can increase the compressive strength by improving the quality of RCA. In carbonation process, CO_2 can enter the pores of the attached mortar, reacting with calcium hydroxide (CH) and hydrated calcium silicate (C-S-H). The carbonation of CH and C-S-H increases the solid volume and thus reduces the porosity of the adhered mortar, which can enhance the quality of RCA and contribute to the strength development of RAC.

From the discussion above, it should be known that both carbonation treatment and TSMA can improve the properties of RAC. The CRAC-2 showed the best strength results which can be attributed to the coupling effect of TSMA mixing approach and carbonation treatment. In addition, the standard deviation of CRAC-2 is the lowest one among that of all concrete mixes, which means that the compressive strength of CRAC-2 is much more stable than that of the other mixes.

3.3.2 Splitting tensile strength

Fig.4 shows the splitting tensile strength of all concrete mixtures including NAC. It can be observed that almost all RAC mixes have a higher splitting tensile strength than that of NAC; the URAC-1 performed worst among the five concrete mixes, with a splitting tensile strength of 3.5 MPa. This can be attributed to the much higher water absorption of RCA without carbonation, followed by weaker interfacial strength between RCA and new mortar matrix because of higher *w/c* around the surface of old attached mortar. The result is in good agreement with previous result[20].

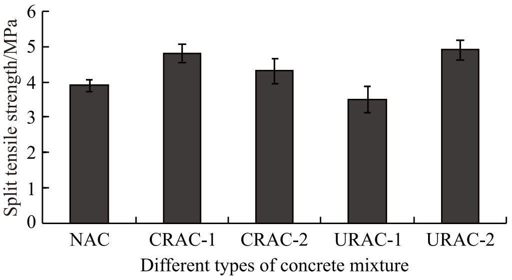

Fig.4 Comparison on splitting tensile strength among different concrete mixtures

It can be found that the splitting tensile strength of URAC-2 is 4.9 MPa, which is 1.4 times as much as that of URAC-1. This indicates that TSMA can significantly improve the splitting tensile strength of RAC. Similarly, the splitting tensile strength of CRAC-1 is 4.8 MPa, which exceeds by 1.3 MPa when compared to URAC-1, which signifies that carbonation treatment of RCA can also increase the splitting tensile strength of RAC. However, the splitting tensile strength of CRAC-2 is not the highest one, which demonstrates that although carbonation treatment or TSMA can separately promote the splitting tensile strength development of RAC, the synergistic effect of carbonation treatment and TSMA may not exist.

3.4 Microstructural analysis of RAC

As mentioned earlier, backscattered electron (BSE) spectroscopy was used to observe the

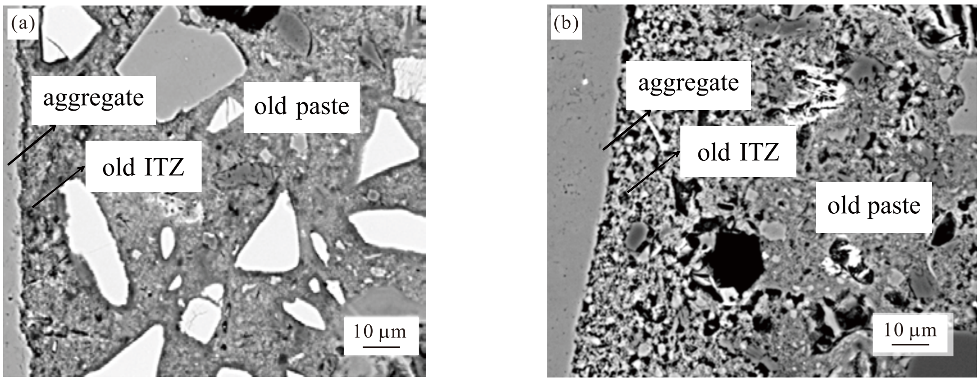

Fig.5 BSE images of microstructure of RAC: (a) Old ITZ microstructure becomes denser in CRAC-2 because of carbonation treatment of RCA; (b) Old ITZ microstructure looks more porous in URAC-2

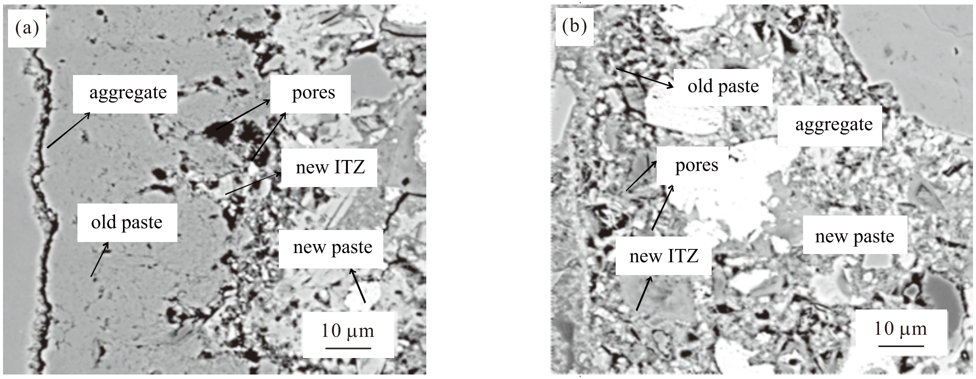

Fig.6 New ITZ microstructure between old paste and new cement paste of RAC: (a) Much more pores and looser microstructure can be seen in new ITZ of CRAC-1; (b) Less pores and much denser microstructure was observed in CRAC-2 due to TSMA in preparing RAC

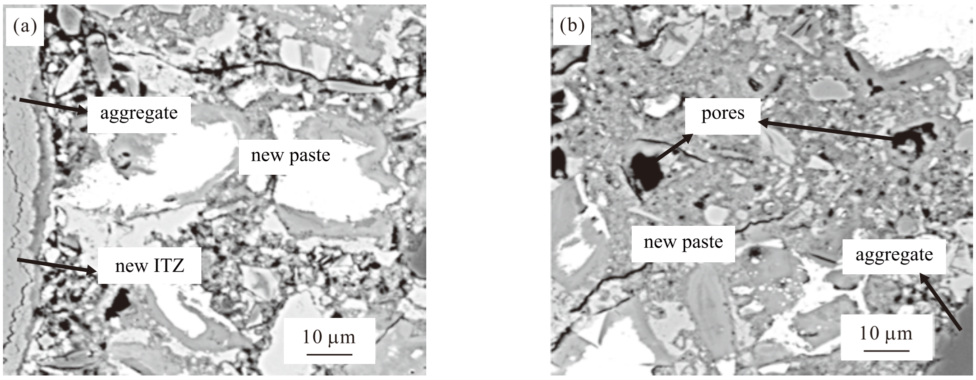

Fig.7 Comparison on microstructure of new cement paste of different RACs: (a) Denser microstructure of new cement paste appears in CRAC-2 because of TSMA in preparing RAC; (b) More pores and cracks can be seen in new paste of CRAC-1

microstructural characteristics of RAC. The left part in Fig.5(a) (uniform grey areas) is natural aggregate, while the right part in Fig.5(a) is old cement paste where there are few anhydrate grains and some glassy substance. The strip area between aggregate and old cement paste is the interfacial transition zone (ITZ) due to the wall effect of aggregates[21]. From Fig.5, it can be seen clearly that the old ITZ in CRAC-2 (Fig.5(a)) is different from the old ITZ in URAC-2 (Fig.5(b)). The ITZ in CRAC-2 shows much denser, while the old ITZ in URAC-2 looks much looser and there are more voids in the attached old paste; this implies that the carbonation treatment of RCA can not only improve the microstructure of attached mortar in RAC, but also modify the microstructure of ITZs due to the fact that CO_2 can react with liquid calcium hydroxide more easily which forms solid calcium carbonate filling the pores and voids of cement paste.

Fig.6 shows the SEM-BSE images of RAC after 28 days of hydration. It is evident that the new ITZ between old paste and new paste in CRAC-1 is much more porous (Fig.6(a)) than that in CRAC-2 (Fig.6(b)). In addition, there are more pores and voids in new ITZ of CRAC-1. This may be attributed to the TSMA which was proved to be effective in modifying the microstructure of concrete[22].In TSMA, half amount of the total required water was added to the mixer and the RCA can absorb the water. There are twofold positive effects. On one hand, there is less water occupying the space in matrix, leading to fewer pores in microstructure of CRAC-2. On the other hand, the water absorbed by RCA in the first stage can further react with the unhydrated cement grains to make the new paste of CRAC-2 much denser.

From Fig.7, it can be found that there is no significant difference between CRAC-2 and CRAC-1 with regard to the hydration products in new cement paste. Nevertheless, there are more pores and cracks in CRAC-1(Fig.7(b)) than in CRAC-2(Fig.7(a)) regarding the microstructure of new paste. In addition, the size of pores in CRAC-1 was found to be a little bigger than that in CRAC-2, which may be because the water in the mixture was absorbed by aggregates nearby during the hydration process. When preparing the concrete with TSMA, one half amount of water was premixed with the RCAs and absorbed. Hence, there was less water occupying the space and reacting with cements, finally leading to few pores in new cement paste, which was consistent with the previous findings[18]. Furthermore, the microstructures of RAC obtained by BSE correspond well with the mechanical properties of RAC in this study.

4 Conclusions

In this paper, the effect of carbonation treatment of RCA on the mechanical properties and microstructure of RAC has been systematically investigated. From the experimental results and discussion above, the following conclusions can be drawn.

A simple set of equipment for accelerating carbonation treatment was successfully applied to improve the quality of RCA. After carbonation treatment, the 24 h water absorption ratio of RCA significantly decreases. This is due to the fact that the content of $CaCO_3$ in attached mortar of RCA increases, which could fill the cracks and voids.

The compressive strength and splitting tensile strength of CRAC are even better than that of control concrete; this signifies that a higher replacement level of NA with RCA should be used, leading to a higher recycling ratio of waste concrete.

In general, the microstructure of CRAC shows much denser than that of URAC. This may contribute to the newly formed solid calcium carbonate during carbonation treatment. And both the new ITZ and old ITZ of CRAC-2 also appear denser when compared to that of CRAC-1 because of TSMA in preparing RAC.

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