

DOI 10.1007/s11595-015-1111-z

Interfacial Interaction of Aggregate-Cement Paste in Concrete

KONG Lijuan^{1,2}, DU Yuanbo¹

(1. School of Materials Science and Engineering, Shijiazhuang Tiedao University, Shijiazhuang 050043, China; 2. Hebei Provincial Key Laboratory of Traffic Engineering Materials, Shijiazhuang 050043, China)

Abstract: The chemical and physical interactions in the interfacial transition zone (ITZ) between three different types of coarse aggregates (limestone, granite and basalt) and cement paste were investigated. The results show that all the aggregates are chemically active. Significant amounts of Ca^{2+} , K^+ , and Na^+ are absorbed by all the aggregates from the cement solution, granite and basalt also absorb significant amounts of OH^- and release significant amounts of Si^{4+} into cement solution. The XRD, EDXA and pore structure results of the ITZ also show that more clinkers participate in the cement hydration in the ITZ of granite and basalt, and more hydrates are generated, hence resulting in a denser ITZ structure with a lower content of macropores. Although the limestone has the least activity, the connection between it and cement paste is tight, due to its rough surface and higher water absorption. Whereas the granite with smooth surface and lower water absorption has a loose connection with cement paste, many pores and cracks are visible, which is very detrimental to the concrete durability.

Key words: aggregate; cement paste; chemical interaction; pore structure

1 Introduction

Concrete has a highly heterogeneous and complex structure. At the microscopic level concrete may be considered to be a three-phase material, consisting of aggregate, cement paste and the interfacial transition zone (ITZ) between them. Many investigations have shown that due to the wall effect and microbleeding, the local water-to-cement ratio (W/C) of the cement paste surrounding aggregate is higher, and the large flat calcium hydroxide (CH) crystals form within this region, perpendicular to the surface of aggregate grains, which results in the formation of a highly porous structure in the cement paste^[1-3], so the ITZ is known to be the weakest region in concrete. Although the thickness of the ITZ is only 40-50 μm , it often becomes the crack origin zone and water permeation way,

influencing both mechanical properties and durability of concrete seriously.

Since it is often assumed that most rock aggregates used in concrete are chemical inert, so there are numerous studies about the influence of cementitious matrix materials (*e.g.*, W/C , use of admixtures, *etc*) on the properties of the ITZ^[4-7], however the influence of aggregate has been given little attention. In fact, the chemical and physical interactions between aggregate and cement paste can influence the development of the microstructure of the ITZ as well. For example, the coarse aggregates with a higher water absorption can reduce the thickness of the water films formed around them, and then improve the microstructure of the ITZ. It has also been found that the alkali-aggregate reaction^[8], which causes a volume change after the concrete has set, significantly affects the concrete durability. Actually the aggregates are more chemically active than has been previously supposed. It was observed that ions are both absorbed and released by the aggregates studied in the aggregate-cement solution systems^[9], which possibly indicates that hydration of the surface layer has taken place. For example, it has been found that a chemical reaction between carbonate aggregate and tricalcium silicate of the cement takes place, and the products yielded can improve the bond strength^[10]. However, Tasong

©Wuhan University of Technology and Springer-Verlag Berlin Heidelberg 2015

(Received: May 19, 2013; Accepted: Oct. 8, 2014)

KONG Lijuan(孔丽娟): Assoc. Prof.; Ph D; E-mail: konglijuan_888@163.com

Funded by the National Nature Science Foundation of China (No. 51108282), Natural Science Foundation of Hebei Province of China (No. E2011210025), Excellent Youth Scholars of University Science and Technology Research of Hebei Province (No. Y2011111), and Hebei Key Discipline Construction Project

et al observed that the limestone reacted with cement paste to produce a very porous ITZ, which resulted in a reduction in bond strength at early age, and chemical reaction between basalt and the cement paste resulted in a reduction of bond strength after 12 weeks of continuous curing^[11]. Moreover, Goguel and John observed that mass transferred from the aggregate to the hydrated phases during concrete hardening by the selective leaching techniques^[12].

In this paper, three typical concrete aggregates, namely limestone, granite and basalt, were chosen for the study. To investigate the interface interaction of aggregate-cement paste, the change of ion in cement solution was tested. Furthermore, the pattern and composition of the hydrates in the ITZ, as well as the pore structure of the paste were analyzed to explore the mechanism of the interaction. The results obtained are expected to enrich our understanding of the role played by aggregate in influencing the development of the microstructure of the ITZ.

2 Experimental

2.1 Materials

Grade 42.5 ordinary Portland cement and Class I fly ash were used in all mixtures. Three types of crushed coarse aggregates were used with particle size between 5 and 20 mm, including limestone from Shijiazhuang, granite from Nanjing and basalt from Lianyungang. The physical properties of the aggregates are summarized in Table 1 and the chemical compositions of cement and coarse aggregates are shown in Table 2. Fine aggregate used was river sand with a

fineness modulus of 2.8 and an apparent density of 2.61 g/cm³. A naphthalene-based superplasticizer was used.

2.2 Mixture proportions

Three groups of concrete mixed with limestone, granite and basalt were prepared, respectively. The water-cement ratio of concrete was 0.49, and the concrete mixture proportions are given in Table 3.

2.3 Specimens preparation and testing

2.3.1 Chemical interaction test

This test used the method described by Tasong^[9]. First, the aggregates were crushed into fine powder, and the cement solution containing Ca²⁺, K⁺, Na⁺, Al³⁺, Si⁴⁺, OH⁻ and other minor ions was obtained. Then 25 g of aggregate powder was suspended in (a) 150 mL of cement solution, and (b) 150 mL of deionised water at 70 °C for various time periods (*i e*, 1, 3, 7, and 28 days). At last, the extracts were taken from the suspensions and analysed for metal ions, sulphur, and hydroxyl ions using inductive coupled plasma (ICP) methods and titration. Comparison of the results with those for the original cement solution (which serves as the control) may indicate a potential aggregate-cement chemical interaction.

2.3.2 Microscopic tests

The coarse aggregates and cement paste were mixed and molded. After 24 h, the specimens were demolded and placed in a standard curing room until the day of testing. Then the specimens were crushed, in the intermediate section the cement paste connected with aggregate was selected to examine the microstructure of the interfacial zone using scanning electron microscope (SEM), and the relative content change of silicon and calcium elements was measured by energy dispersive X-ray analysis (EDXA). After

Table 1 Physical properties of coarse aggregate

Types	Packing density/(kg/m ³)	Apparent density/(kg/m ³)	Compressive strength/MPa	Water absorption/%
Limestone	1 520	2 640	65	0.9
Granite	1 710	2 860	148	0.3
Basalt	1 650	2 730	112	0.4

Table 2 Chemical compositions of cement and coarse aggregates obtained using XRD/wt%

Compositions	SiO ₂	TiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	P ₂ O ₅	Loss
Cement	22.21	0.01	2.78	5.32	63.81	2.28	1.23	0.27	0.38	0.02	1.06
Limestone	4.56	0.02	0.87	0.12	52.99	0.78	0.92	0.05	0.02	0.01	39.53
Granite	79.13	0.17	2.13	11.63	2.48	0.01	0.28	1.68	0.01	0.01	2.08
Basalt	48.56	2.25	14.16	14.26	8.75	4.17	0.08	2.16	0.91	0.12	2.83

Table 3 Mixture proportions of concrete

Aggregate types	Water/(kg/m ³)	Cement/(kg/m ³)	Sand/(kg/m ³)	Crushed stone/(kg/m ³)	Fly ash/(kg/m ³)	UNF-5/%
Limestone	160	278	687	1 154	64	0.45
Granite	160	278	687	1 250	64	0.45
Basalt	160	278	687	1 193	64	0.45

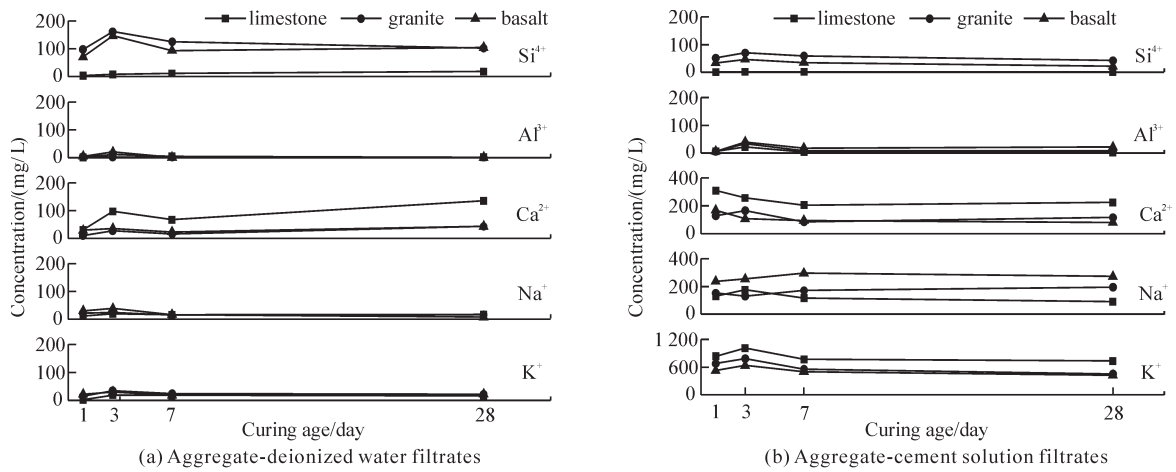


Fig.1 Changes in concentration of ions in filtrates with curing age

flaking off the coarse aggregate, the cement paste located within 3 mm from the aggregate surface was obtained. A sample of the paste was analyzed using a mercury intrusion porosimetry (MIP) to investigate the pore structure. The sample was also ground using agate mortar for the X-ray diffraction (XRD) analysis.

3 Results and discussion

3.1 Chemical interaction of aggregate-cement

The changes in concentration of cations in aggregate-deionized water filtrates and aggregate-cement solution filtrates are shown in Fig.1. The graph shown in Fig.2 is the result of the changes in concentration of OH⁻ in the original cement solution and aggregate-cement solution filtrates with curing age. Three specimens were tested for each result, and the average is presented.

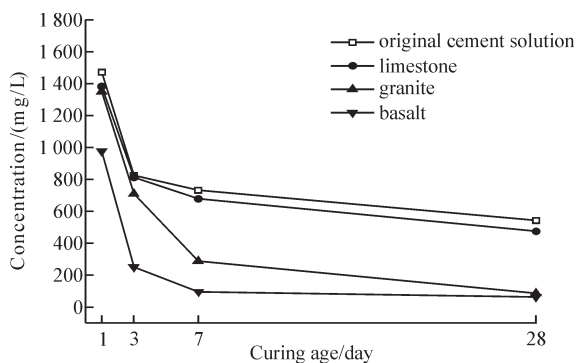


Fig.2 Changes in concentration of OH⁻ in the original cement solution and aggregate-cement solution filtrates with curing age

From the results shown in Fig.1(a), limestone released very significant amounts of Ca²⁺ and minor amounts of K⁺, Na⁺, Al³⁺ and Si⁴⁺ into the deionized water. Granite and basalt released very significant amounts of Si⁴⁺, significant amounts of Ca²⁺, and

minor amounts of K⁺, Na⁺ and Al³⁺ into the deionized water. This indicates that the hydration of the surface layer of the aggregates has taken place. In general, the results showed an increase in ion concentration during the first 3 days, followed by a fall at 7 days, then the concentrations stayed fairly constant right up to 28 days. The drop in concentration at 7 days may indicate the growth of a secondary mineral.

Fig.1(b) and 2 show that all the types of aggregates absorbed very significant amounts of Ca²⁺, K⁺ and Na⁺ from the cement solution. Both granite and basalt also absorbed significant amounts of OH⁻ and released significant amounts of Si⁴⁺ into cement solution, however limestone had little effect on the concentrations of the remaining ions. This probably indicates the formation of hydrated calcium silicates as well as feldspars on the surface of aggregate particles.

From the results presented above it can be seen that all the aggregates studied showed chemical activity. Although the cement solution used in this investigation is lower in concentration than that expected in cement paste pore fluid, the chemical interaction of aggregate-cement paste in the ITZ can be identified.

3.2 XRD patterns of hydrates in the ITZ

From the XRD patterns of interfacial hydrates around different types of aggregates shown in Fig.3, it can be seen that the hydrates products for different cases are similar. There are mainly CH, AFt and some unhydrated clinkers of C₃S and C₂S. The amorphous C-S-H can hardly be observed in the XRD pattern. In the specimen around limestone, the most amounts of C₃S can be observed, whereas the specimen around basalt has little unhydrated clinkers of C₃S and C₂S. This could suggest that in the ITZ of granite and basalt, more clinkers participate in the hydration of cement, and more hydrates are generated. This may also demonstrate that the basalt and granite have more chemical activity than the limestone.

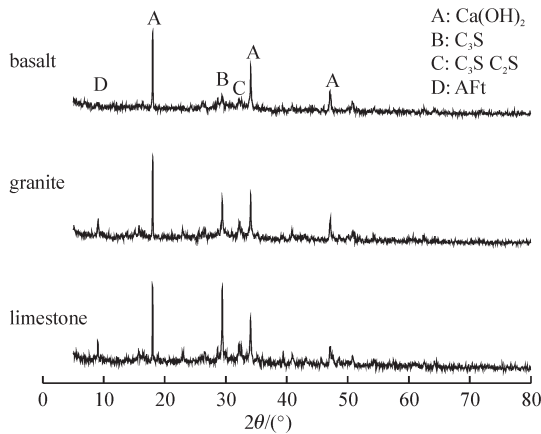


Fig.3 XRD patterns of interfacial hydrates around different types of coarse aggregates

3.3 SEM and EDXA study of hydrates in the ITZ

The interaction of aggregate-cement paste in the ITZ can also be testified by the SEM observation at 28 days, as shown in Fig.4.

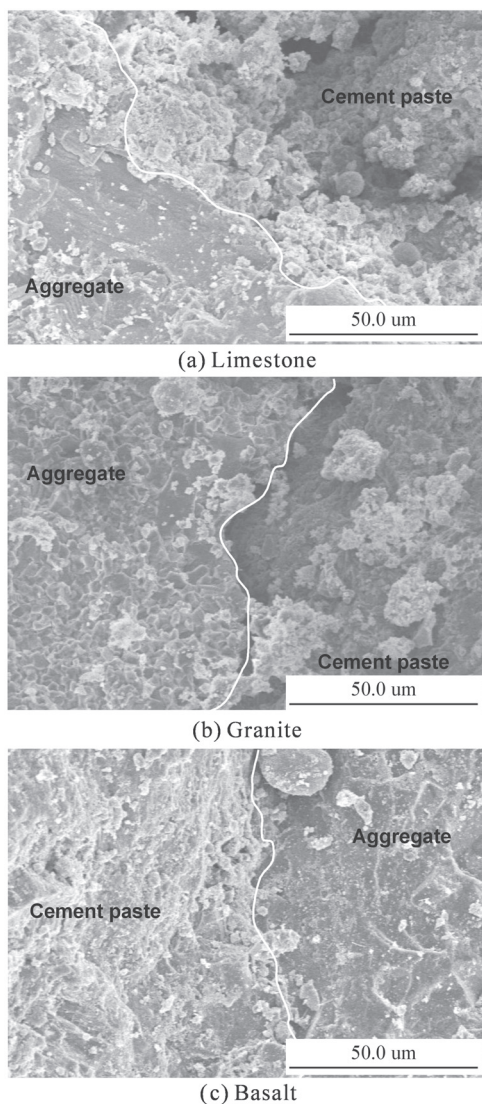


Fig. 4 Effect of coarse aggregate types on microstructure of the ITZ

From Fig.4(a) it is seen that the microstructure of the cement paste around limestone is loose, and some pores with micron dimension can be observed. However, there is a tight connection between the aggregate and cement paste, which may be due to the higher water absorption and rough surface of limestone. The microstructure of the paste around granite and basalt is denser than that of limestone, little pores and flaws can be seen, many cluster hydrates are closely packed together, and lithic gels are formed. So it becomes difficult to identify the paste and aggregate from the pattern, as shown in Figs.4 (b) and (c). This is consistent with the results showed in Fig.3. However, there is a loose interface between granite and paste, many pores and cracks is visible clearly, which is account for the smooth surface and lower water absorption of granite, and hence the resultant weak physical interaction between aggregate and cement paste. Moreover, the reaction traces can be observed from the surface of all the three types of aggregates, which also demonstrates the existence of a chemical reaction between aggregate and cement paste.

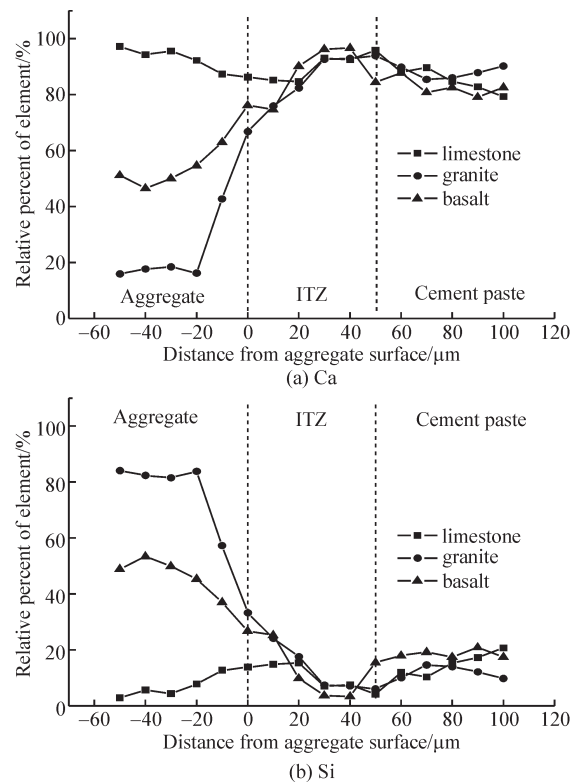


Fig.5 Element analysis of the ITZ around different types of coarse aggregate

Besides, the specimens with three different types of coarse aggregates were measured using EDXA, and the results represented the mixture of multi-hydrates are shown in Fig.5. The data were obtained at 10 μm intervals from the aggregate to bulk cement paste,

and each point in the figure was the average of 10 test points. In abscissa axis, zero represents the interface between coarse aggregate and cement paste.

From the elemental analysis results as shown in Fig.5, the granite is silicon-rich phase, and the limestone is calcium-rich phase. The ITZ range of all the three types of coarse aggregates is about 50 μm . In the aggregates near the interface region, the relative percent of elements starts to change, such as the silicon content of granite and basalt, as well as calcium content of limestone all have a falling at the distance of 20 μm from the interface. This indicates that there are chemical interactions between cement paste and all the three types of aggregates. Moreover, from the interface to the 20 μm region of the ITZ, the silicon contents of granite and basalt are higher than that of limestone, as shown in Fig.5(b), which demonstrates that more hydrated calcium silicates are generated in the ITZ of the two igneous rocks. However, more calcium hydroxide and ettringite form in the ITZ of limestone, as shown in Fig.5(a).

3.4 Pore structure of hydrates in the ITZ

The pore structure of the cement paste surrounding different types of coarse aggregates at 28 days was measured, and the pore structure parameters of specimens are summarized in Table 4.

Sample	Porosity /%	Pore volume content/%			
		<10 nm	10-100 nm	100-1 000 nm	>1 000 nm
Limestone	26.87	17.07	55.70	20.59	6.64
Granite	28.69	16.68	67.29	10.87	5.16
Basalt	27.27	16.19	63.13	15.06	5.62

The results in Table 4 show that the porosity of the specimens around limestone is the lowest, which may be due to its higher water absorption. However, the volume content of the macropore of the specimens around granite and basalt is lower than that of the specimen around limestone, especially for the macropore from 100 nm to 1 000 nm. For instance, compared to the specimen around limestone, the macropore content of the specimen around granite in the range of 100-1 000 nm is reduced by 47.2%. This may account for the chemical interaction between the aggregates and cement paste, so in the specimens around granite and basalt more hydrates are generated, filling into the pores and making the pore structure of cement paste finer.

From the results presented above it can be seen that both chemical and physical interactions have taken place in the ITZ, therefore the cementing bond between aggregate and cement paste, as well as the hydrates and microstructure of the ITZ can be affected.

4 Conclusions

a) All the aggregates studied showed chemical activity. Significant amounts of Ca^{2+} , K^{+} and Na^{+} are absorbed by all the aggregates from the cement solution, granite and basalt also absorbed significant amounts of OH^{-} and released significant amounts of Si^{4+} into cement solution. In this respect, limestone is the least active aggregate.

b) From the XRD, EDXA and pore structure results of the ITZ around different types of aggregates, it can be seen that more clinkers participate in the cement hydration in the ITZ of granite and basalt and more hydrates are generated, which is consistent with the chemical interaction results, hence resulting in a denser ITZ structure with a lower content of the macropores.

c) The physical interaction between aggregate and cement paste mainly depends on the surface roughness and water absorption of the aggregate. In this study, there is a tight connection between limestone and cement paste. Although the microstructure of the paste around granite is denser, the connection between granite and paste is loose, which is very detrimental to the concrete durability.

References

- [1] Elsharief A, Cohen M D, Olek J. Influence of Aggregate Size, Water Cement Ratio and Age on the Microstructure of the Interfacial Zone[J]. *Cement and Concrete Research*, 2003, 33(11): 1 837-1 849
- [2] Belaid F, Arliguie G, Francois R. Porous Structure of the ITZ Around Galvanized and Ordinary Steel Reinforcement[J]. *Cement and Concrete Research*, 2001, 31(11): 1 561-1 566
- [3] Scrivener K L. Backscattered Electron Imaging of Cementitious Microstructures: Understanding and Quantification[J]. *Cement and Concrete Composites*, 2004, 26(8): 935-945
- [4] Huo J F. Effect of Silica Fume and Fibers on Frost Resistance Durability of Lightweight Aggregate Concrete[J]. *Journal of Wuhan University of Technology*, 2008, 30(11): 65-68
- [5] Rangaraju P R, Olek J, Diamond S. An Investigation into the Influence of Inter-Aggregate Spacing and the Extent of the ITZ on Properties of Portland Cement Concrete[J]. *Cement and Concrete Research*, 2010, 40(11): 1 601-1 608
- [6] Xuan D X, Shui Z H, Wu S P. Influence of Silica Fume on the Interfacial Bond between Aggregate and Matrix in Near-Surface Layer of Concrete[J]. *Construction and Building Materials*, 2009, 23(7): 2 631-2 635
- [7] Jiang L H. The Interfacial Zone and Bond Strength between Aggregate and Cement Paste Incorporating High Volumes of Fly Ash[J]. *Cement and Concrete Composites*, 1999, 21(4): 313-316
- [8] Hu K, Wang H M, Wang Y M. Investigation into Influences of Alkali-Aggregate Responses on Concrete Durability[J]. *Journal of Heilongjiang Hydraulic Engineering College*, 2005, 32(4): 53-55
- [9] Tasong W A, Cripps J C, Lynsdale C J. Aggregate-Cement Chemical Interaction[J]. *Cement and Concrete Research*, 1998, 28(7): 1 037-1 048
- [10] Monteiro P J M, Metha P K. Interaction between Carbonate Rock and Cement Paste[J]. *Cement and Concrete Research*, 1986, 16(2): 127-134
- [11] Tasong W A, Lynsdale C J, Cripps J C. Aggregate-Cement Paste Interface Part I. Influence of Aggregate Geochemistry[J]. *Cement and Concrete Research*, 1999, 29(10): 1 019-1 025
- [12] Goguel R L, St John D A. Chemical Identification of Portland Cements in New Zealand Concretes: II The Ca Sr Mn Plot in Cement Identification and the Effect of Aggregates[J]. *Cement and Concrete Research*, 1993, 23(2): 283-290