Influence of siliceous material on durability of GRC based on Portland cement

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Summary

This paper examines the influence of several siliceous materials such as microsilica, metakaolin or ground granulated blastfurnace slag (ggbs) on the durability of glassfibre-reinforced concrete (GRC) based on Portland cement. It reports the change in mechanical properties of different GRC formulations, through testing the flexural strength and impact strength of GRC subjected to accelerated aging for different periods. Additionally, microscopic examination is undertaken to validate the degeneration mechanisms of mechanical properties of GRC.

Test results indicate that GRC durability is improved to a certain extent when cement is substituted partially by 20% microsilica or 30% metakaolin, and that GRC durability is improved most markedly when cement is substituted partially by 20% microsilica and 10% metakaolin. In this study, we also find that ggbs has little influence on GRC durability, even when substituting cement by to 50%.

Key words: microsilica, metakaolin, ggbs, Portland cement, GRC, durability

1. Raw materials and formulation

1.1. Raw materials

Cement: grade 42.5, ordinary Portland cement; its properties are listed in Table 1.

Setting time (min.)		Compressive strength (MPa)		Flexural strength (MPa)	
Initial setting	Final setting	3 day	28 day	3 day	28 day
120	200	26.2	47.5	6.52	8.13

Table 1. Properties of ordinary Portland cement

Microsilica: specific surface area is 20 000 m^2/kg; chemical components are listed in Table 2.

Chemical ingredient	SiO_2	ZrO_2	Fe_2O_3	Al_2O_3	Na_2O	K_2O	TiO_2
Content (%)	≥ 88	6–10	≤ 0.4	≤ 0.5	≤ 0.05	≤ 0.02	≤ 0.05

Table 2. Chemical profile of microsilica

Metakaolin: Its technical properties and chemical components are listed in Table 3.

Retained percentage (180 sieve)(%)	LOI (%)	Chemical ingredients (%)			
		SiO_2	Al_2O_3	Fe_2O_3	TiO_2
0.03	0.24	54.68	42.41	0.21	0.20
LOI = loss on ignition.					

Table 3. Technical properties and chemical ingredients of metakaolin

Ground granulated blastfurnace slag: Its chemical ingredients are listed in Table 4.

Chemical ingredient	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	SO_3	LOI
Content (%)	33.27	12.10	38.39	11.18	1.63	0.15	≤ 3.0

Table 4. Chemical ingredients of ggbs

Alkali-resistant (AR-)glassfibre: this was obtained from two producers; the ZrO_2 content for both was 16.7%.

Sand: river sand, maximum grain size 2 mm; fines content not more than 2%.

Admixture: superplasticiser,.

Water: tap water.

1.2. GRC formulation

The water/cement (w/c) ratio was 0.4:1; cement/sand ratio was 1:1 of matrix mortar; the fluidity of the mortar mixture was controlled by adjusting the dosage of superplasticiser. Table 5 lists the GRC formulation studied in this paper.

Serial No.	Cement	Siliceous material			Glassfibre type
		Microsilica	Metakaolin	ggbs	
P-A	100				A
Bfs-A-1	70			30	A
Bfs-A-2	50			50	A
MK-A	70		30		A
P-B	100				B
Si-B	80	20			B
MK-Si-B	70	10	20		B

Table 5. GRC formulation (wt%)

It was observed from experiments that water retention of the mixture was not good, and there was little bleeding when ggbs was added. It was also observed that large quantities of superplasticiser had to be added to obtain a suitable fluidity for spray when microsilica and metakaolin were used together.

2. Test procedure

2.1. Preparation of GRC sample

Several test panels measuring 800 × 600 × 10 mm were made by means of the spray method. These panels were cured for 28 days at room temperature, then samples were cut from the panels. Sample size for flexural testing was 250 × 50 × 10 mm; sample size for impact testing was 120 × 50 × 10 mm. The flexural and the impact samples were each collated into groups of ten. Some of these groups were accelerated in water at a temperature of 80°C; others were kept in a natural environment in Beijing for the designated aging period.

2.2. Test method

2.2.1. Flexural strength. GRC samples were removed from the aging condition and dried for three days at room temperature. Flexural testing was then carried out by a WD4100 electronic testing machine, in third-point loading , with a span of 210 mm and a loading speed of 5 mm/min. The limit of proportionality (LOP) and modulus of rupture (MOR) were recorded.

2.2.2. Impact strength. GRC samples were removed from aging condition and dried for three days at room temperature, then impact testing was carried out by an XCJ-50 Charpy impact machine. The impact energy was recorded.

2.2.3. Observation of glassfibre surface. A broken sample piece was placed immediately in pure alcohol. Prior to observation a surface layer of GRC was removed and a small sample measuring 1 cm^3 was taken. The surface needed to be fresh and contain cement hydration products and glassfibre. The surface of the sample was studied by scanning electronic microscopy.

2.2.4. Test of $Ca(OH)_2$ intensity. The sample was made from paste, having a w/c ratio of 0.5. Aging condition and aging time were the same as for the samples used for testing mechanical properties. After the designed aging time was achieved, the sample was removed, dried, and a core taken; the core was then placed immediately in alcohol. Prior to testing, the sample was removed from the alcohol and XRD analysis was then carried out.

3. Test results and discussion

3.1. Test results of mechanical properties

3.1.1. Mechanical properties of GRC in natural environment. The test results of flexural strength for various formulations of GRC in a natural environment are listed in Table 6, and the test results of impact strength for various GRC formulations are listed in Table 7.

Ageing time (days)	P-A	Bfs-A-2	MK-A	P-B	Si-B	MK-Si-B
0	18.0	22.5	21.4	16.9	32.8	28.6
28	17.3	19.7	20.2	15.0	29.4	24.5
56	17.4	20.0	19.1	15.9	30.6	24.6
90	16.8	18.8	18.8	15.3	29.3	25.7
180	15.2	19.2	17.7	15.0	30.4	24.3
Note: Ageing time means time ageing in natural environment after 28 days' standard curing.						

Table 6. Test results of flexural strength (MPa) for GRC in natural environment

As can be seen from Table 6, microsilica can clearly increase the flexural strength of GRC. In the case of no aging, compared with the control group P-A, the flexural strength of GRC with ggbs increases 25% whereas that of GRC with metakaolin increases 18%. Compared with the control group P-B, the flexural strength of GRC with microsilica increases 94%, and that of GRC with microsilica and metakaolin increases 70%. It is apparent that, with regard to increase of flexural strength, the effect of microsilica is more marked than for both metakaolin and ggbs.

After a period of time, the flexural strength of all formulations of GRC decreases, but only to a small degree within the experimental period. When using A-type AR-glassfibre, the flexural strength of GRC without siliceous material decreases by 15.6%; the flexural strength of GRC with 50% ggbs decreases by 14.7%; and the flexural strength of GRC with 50% metakaolin decreases by 17.3%. All the GRC samples are stored in a natural environment for 180 days. When using B-type AR-glassfibre, the flexural strength of GRC without siliceous material decreases by 11.2%; the flexural strength of GRC with 20% microsilica decreases by 7.3%; and the flexural strength of GRC with 30% metakaolin and 10% microsilica decreases by 15.0%. All the GRC samples are stored in a natural environment for 180 days.

Ageing time (days)	P-A	Bfs-A-2	MK-A	P-B	Si-B	MK-Si-B
0	16.5	18.3	20.1	13.3	23.3	21.3
28	16.3	18.0	18.8	12.0	23.2	21.2
56	16.0	17.9	19.0	11.7	22.6	21.0
90	16.4	16.3	18.9	11.6	22.4	20.9
180	15.9	15.6	16.4	11.0	21.7	19.9
Note: Ageing time means time ageing in natural environment after standard 28-day curing.						

Table 7. Test results of impact strength of GRC in natural environment

It can be seen from Table 7 that after a period of time the impact strength of all formulations of GRC follow a decreasing trend. Microsilica has the obvious effect of increasing impact strength, in case of no aging, compared with the control group P-A; the impact strength of GRC with ggbs increases by 10%; that of GRC with metakaolin increases by 20%; compared with the control group P-B, the impact strength of GRC with microsilica increases by 70%; and that of GRC with microsilica and metakaolin increases by 60%. It can be seen from these observations that, as regards increase in impact strength, the effect of microsilica is more pronounced than metakaolin and ggbs.

3.1.2. Mechanical properties of GRC accelerated in 80°C water. Test results of flexural property for GRC accelerated in 80°C water are listed in Tables 8 and 9.

Ageing time (days)	P-A		Bfs-A-1		Bfs-A-2		MK-A	
	LOP	MOR	LOP	MOR	LOP	MOR	LOP	MOR
0	8.4	20.7	9.5	19.4	7.5	18.4	8.4	18.6
1	9.5	17.3	11.0	15.7	8.3	16.9	8.6	18.5
3	9.0	16.3	7.3	14.2	8.1	16.3	9.3	17.4
7	10.1	13.1	10.2	12.5	8.6	11.4	7.8	16.1
9	11.2	12.6	8.9	12.1	8.9	12.5	10.5	14.9
12	8.3	11.8	9.7	12.0	9.2	11.0	10.0	13.5
14	12.9	12.9	11.3	11.3	11.2	11.7	9.8	13.2
16	12.7	12.7	11.3	11.3	10.6	10.6	8.8	13.3
18							10.6	13.1
21							10.1	13.1
28							9.0	13.0
39							10.9	12.9
Note: Ageing time means time ageing in 80°C water after standard 28-day curing.								

Table 8. Test results of flexural property for GRC accelerated in 80°C water (A-type glassfibre)

Ageing time (days)	P-B		Si-B		MK-Si-B	
	LOP	MOR	LOP	MOR	LOP	MOR
0	8.3	18.1	9.5	28.9	6.2	22.2
1	8.9	16.8	8.7	27.1	7.6	22.2
3	10.5	15.1	9.1	25.0	7.6	21.9
7	8.7	11.1	11.3	19.9	11.1	18.1
9	10.3	11.8	9.1	16.6	11.0	18.9
12	7.6	9.1	9.8	17.0	9.7	15.8
14	10.1	11.1	8.7	16.7	10.5	15.5
16	9.8	9.8	8.1	14.4	9.5	15.3
18			11.0	15.1	9.6	15.0
21			8.2	14.0	8.7	14.8
28			11.4	16.0	11.4	14.3
39			12.2	15.1	11.5	14.3
Note: Ageing time means time in 80°C water after 28-day standard curing.						

Table 9. Test results of flexural property for GRC accelerated in 80°C water (B-type glassfibre)

In fact, it may be considered that glassfibre lost its reinforcement effect completely when flexural MOR of GRC decreased to be equal to its LOP. It can be seen from Tables 8 and 9 that glassfibre loses its reinforcement effect when GRC samples are subjected to accelerated aging for 14 or 16 days in 80°C water; these GRC samples are formed with two separate types of AR-glassfibre. During the experiments, it was observed that in their initial status GRC samples broke in the form of multiple cracks and that glassfibre still retained its high strength. However, at the end of the aging period GRC samples broke in the form of single cracks and the glassfibre had very little strength.

Figure 1 shows the pattern of change for the flexural MOR of GRC specimens subjected to accelerated aging; these GRC samples were made of A-type glassfibre combined with a different matrix.

Two things can be seen from Figure 1. First, that compared with the control group P-A, the rate of reduction of flexural strength of GRC samples with metakaolin was relatively slower; retention of flexural strength of GRC aged for 14 days in 80°C water was still 72.6%; subsequently, with the passage of time, flexural strength was maintained at approximately 13 MPa, which is 3–4 MPa higher than the LOP; and there remained a certain increase in effect after the addition of AR-glassfibre aged for 39 days in 80°C water, which shows that metakaolin can effectively improved the long-term performance of GRC.

Second, the rate of reduction of flexural strength of GRC with ggbs was almost equal to that of the control group P-A; the flexural strength of GRC aged for 14 days in 80°C water reduced to the flexural strength of the GRC matrix of GRC, i.e. the LOP of GRC.

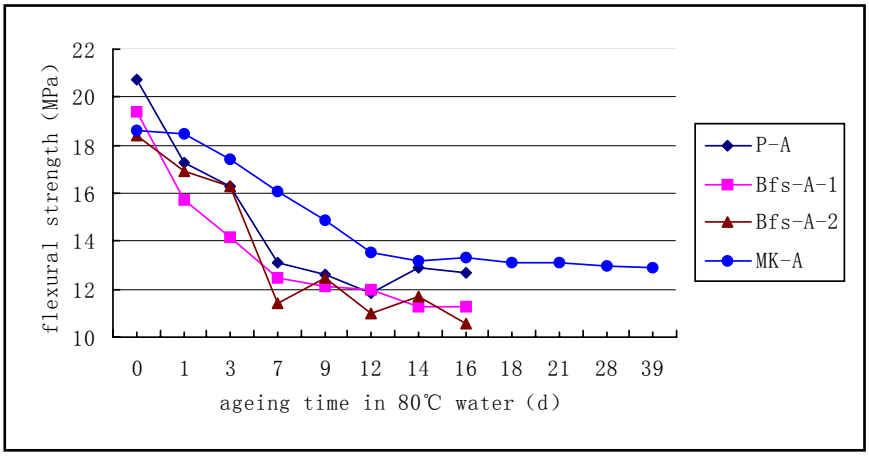

Figure 1. Flexural strength of GRC（A-type glasfibre） subjected to accelerated ageing in 80°C water plotted against aging time

By this time the effect of AR-glassfibre had reduced completely which shows that the ggbs used in this experiment cannot improve the long-term performance of GRC.

Figure 2 shows the trend of flexural strength of GRC aged in 80°C water and made with B-type AR- glassfibre combined with different matrices.

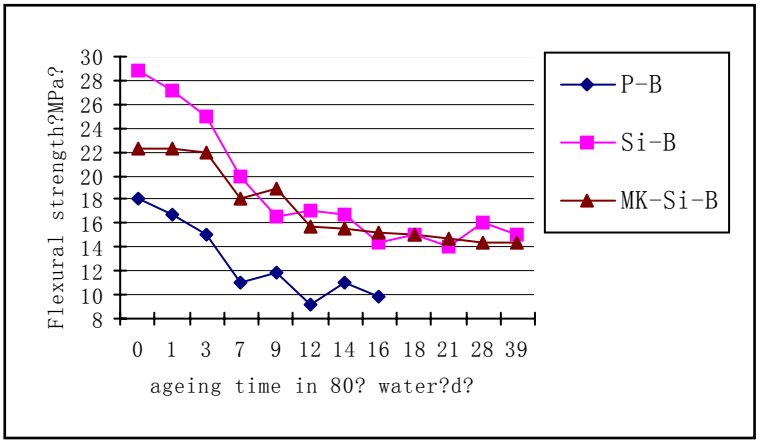

Figure 2. Flexural strength of GRC（using B-type glassfibre）subjected to accelerated ageing in 80°C water plotted against ageing time

Figure 2 highlights three points. First, that compared with control group P-B, the flexural strength of GRC increased significantly at all ages when adding microsilica or microsilica and metakaolin. Second, that compared with control group P-B, the rate of flexural strength reduction of GRC with microsilica was relatively faster when GRC was aged for nine days in 80°C water, and that of GRC with microsilica and metakaolin was relatively slower; the P-B formulation GRC reduced by 34.8%, the Si-B formulation GRC reduced by 42,6% and the MK-Si-B formulation reduced by 30.2%. Third, comparing the matrix with microsilica with that of microsilica and metakaolin, the rate of flexural strength reduction of the former was initially faster; both GRC mixtures maintained their strength at a higher level from 12 to 39 days' aging; moreover, the flexural strength of both mixtures tended to be equal. This indicates that adding microsilica alone or microsilica and metakaolin simultaneously can effectively improve long-term performance.

Test results of impact strength for GRC subjected to accelerated ageing in 80°C water are given in Table 10. Figures 5 and 6 show the trend for impact strength of GRC subjected to accelerated ageing in 80°C water.

Ageing time (days)	P-A	Bfs-A-1	Bfs-A-2	MK-A	P-B	Si-B	MK-Si-B
0	16.1	16.0	18.4	18.8	13.4	23.9	19.9
1	12.6	10.8	12.8	21.3	11.2	19.3	17.1
3	11.8	7.4	9.1	12.4	8.1	14.9	16.4
7	3.3	3.3	3.3	7.2	3.3	7.6	8.5
9	3.3	2.5	3.1	5.6	3.1	6.0	7.1
12	2.4	2.4	2.9	3.6	3.1	4.7	6.2
14	2.4	2.5	2.5	5.2	2.8	4.9	5.2
16	2.3	2.2	2.5	4.1	2.5	4.7	5.6
18				3.9		5.2	5.8
21				3.8		3.6	4.6
28				3.6		4.2	4.0
39				3.8		4.0	4.0
Note: Ageing time means time ageing in 80°C water after 28-day standard curing.							

Table 10. Impact strength of GRC subjected to accelerated ageing in 80°C water

It can be seen from Table 10 that the impact strength of GRC for all the formulations largely decreased when GRC was aged in 80°C water for three days.

For GRC using A-type glassfibre, when GRC was aged for three days, the impact strength of GRC for control group P-A reduced by 26.7%; the impact strength of GRC with 30% ggbs reduced by 53.8%; the impact strength of GRC with 50% ggbs reduced by 50.5%; and the impact strength of GRC with 30% metakaolin reduced by 34.0%. When GRC was aged for seven days, the impact strength of GRC for all the formulations reduced sharply: the impact strength of GRC for control P-A reduced by 79.5%; the impact strength of GRC with 30% ggbs reduced by 79.4%; the impact strength of GRC with 50% ggbs reduced by 82.1% and the impact strength of GRC with 30% metakaolin reduced by 60.9%. Subsequently, the impact strength of different formulations of GRC reduced to a steady value at different ageing times respectively; the final impact strength of the control group GRC and GRC with ggbs was 2.2–2.5 kJ/m^2 but the impact strength of GRC with metakaolin was still 3.8 kJ/m^2 when aged for 39 days, which indicates that metakaolin has a better effect on delaying the brittleness of GRC.

For GRC using B-type glassfibre, when GRC was aged for three days, the impact strength of control group P-B GRC reduced by 39.6%; the impact strength of GRC with 20% microsilica reduced by 37.7%; the impact strength of GRC with 10% microsilica and 20% metakaolin reduced by 17.6%. When GRC was aged for seven days, the impact strength of all formulations of GRC reduced sharply; the impact strength of control group P-B GRC reduced by 75.4%; the impact strength of GRC with 20% microsilica reduced by 68.2%; the impact strength of GRC with 10% microsilica and 20% metakaolin reduced by 57.3%. Subsequently, the impact strength of different formulations of GRC reduced to a steady

value at different ageing times respectively; the final impact strength of control group GRC was 2.5 kJ/m^2, but the impact strength of GRC with microsilica and metakaolin aged for 39 days was still 4.0 kJ/m^2, which indicates that microsilica has a better effect on delaying the brittleness of GRC. Figures 3 and 4 show the trend of impact strength of GRC with A-type or B-type glassfibre.

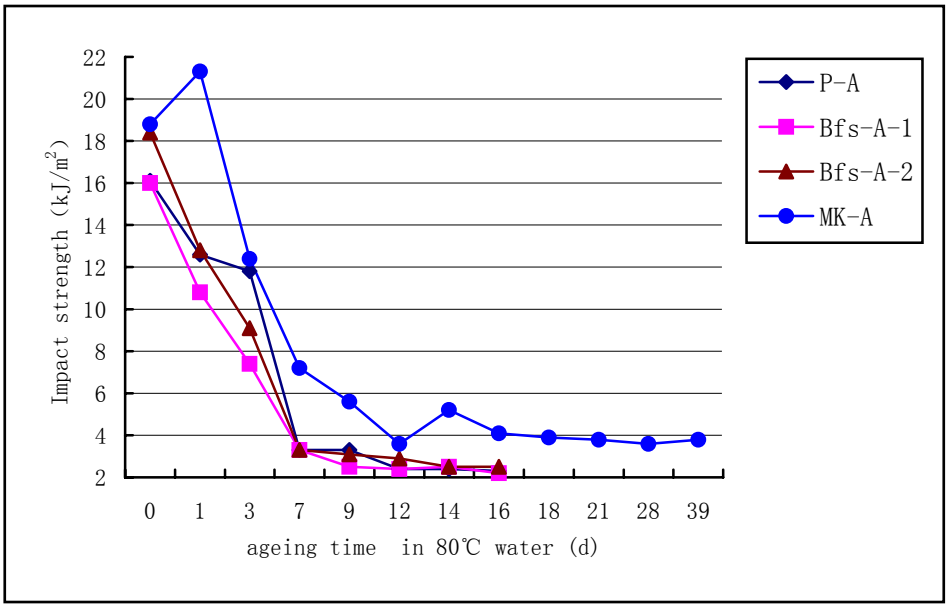

Figure 3. Impact strength of GRC（A-type glassfibre）subjected to accelerated ageing in 80℃ water plotted against ageing time

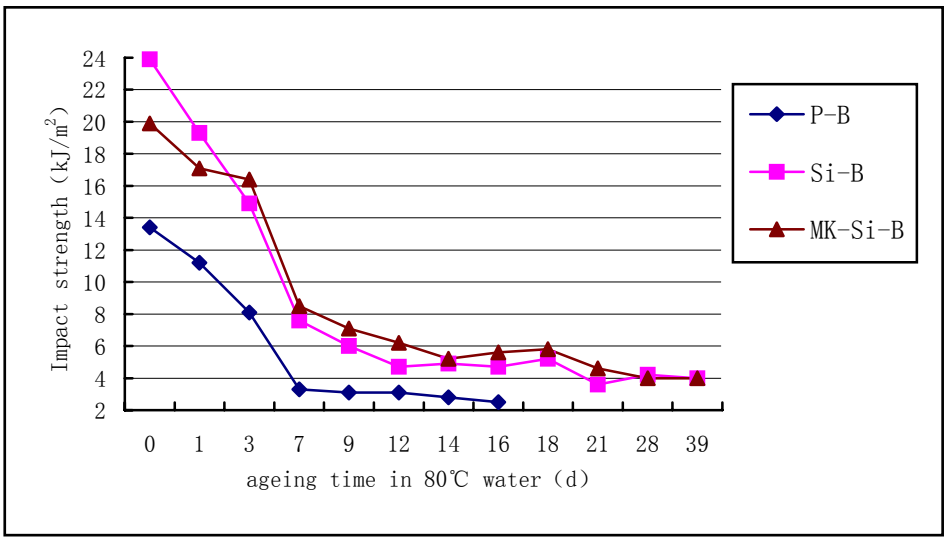

Figure 4. Impact strength of GRC（B-type glassfibre）subjected to accelerated ageing in 80℃ water plotted against ageing time

3.2. Observation results on surface of glassfibre

The surface modality of glassfibre observed with a scanning electron microscope is shown in Figures 5–8.

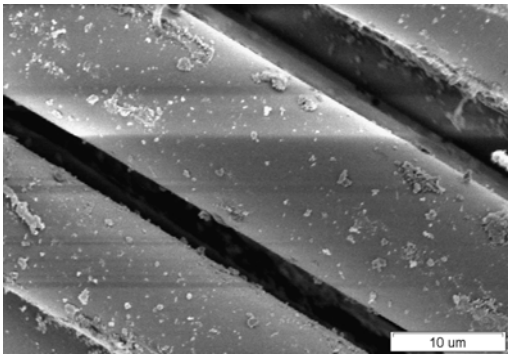

Fig.5 P-A (standard curing,28 days)

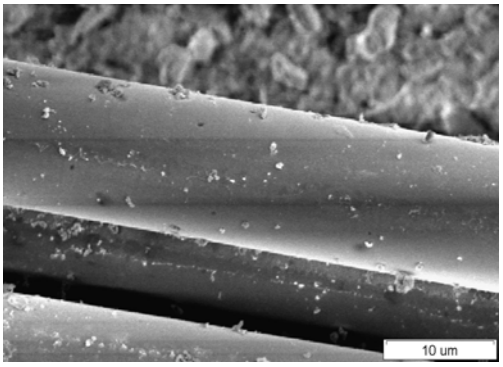

Fig.6 MK-A (in 80 ℃ water,14 days)

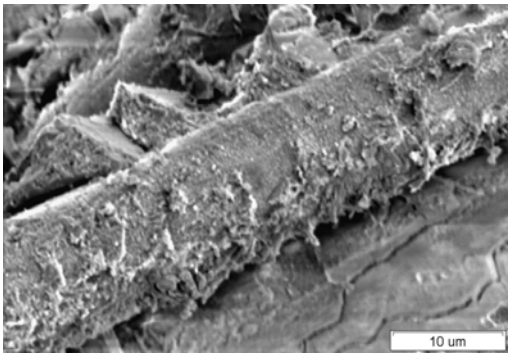

Fig.7 P-A (in 80 ℃ water,14 days)

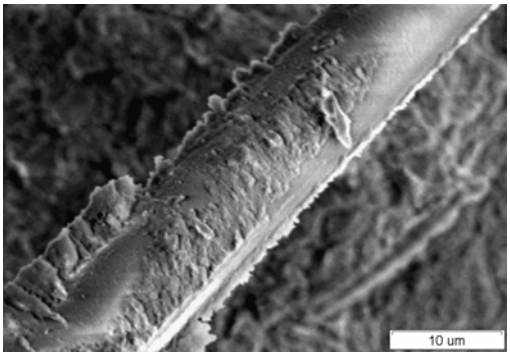

Fig.8 MK-A (in 80 ℃ water,39days)

Comparing Figure 5 with Figure 7, when GRC has been cured at standard condition for 28 days, the outline of glassfibre is still clear and there is little substance attached to its surface. Conversely, when GRC is cured in 80°C water for 14 days, the glassfibre is subject to serious corrosion and there is a large quantity of substance attached to its surface.

Comparing Figure 6 with Figures 7 and 8, when GRC with metakaolin is cured in 80°C water for 14 days, the fibre is mostly not corroded and there is a small amount of substance attached to its surface. When GRC is cured in 80°C water for 39 days, there is substance attached to its surface but its outline is still clear. However, for GRC cured in 80°C water for 14 days, the outline of the fibre is no longer clear.

3.3. Analytic results of $Ca(OH)_2$ crystal content in hydration product

By analysis using X-ray diffraction (XRD), the hydration products of hardened cement paste correspond to different GRC formulations.

Figure 9 shows the XRD pattern of hydration product of ordinary Portland cement; its hydration products include C-S-H, Aft and $Ca(OH)_2$ etc.; its crystal products AFt and $Ca(OH)_2$ are tested by XRD. It is seen from the pattern of the sample cured in standard condition and the pattern of the sample aged in hot water that the peak value of $Ca(OH)_2$ is sharper with increased ageing, which indicates that the quantity of $Ca(OH)_2$ is proportional to the length of accelerated ageing in hot water. The peak of AFm is seen in the pattern of samples aged in 80°C water, but the peak is not seen in the pattern of samples cured at standard condition and aged in 50°C water.

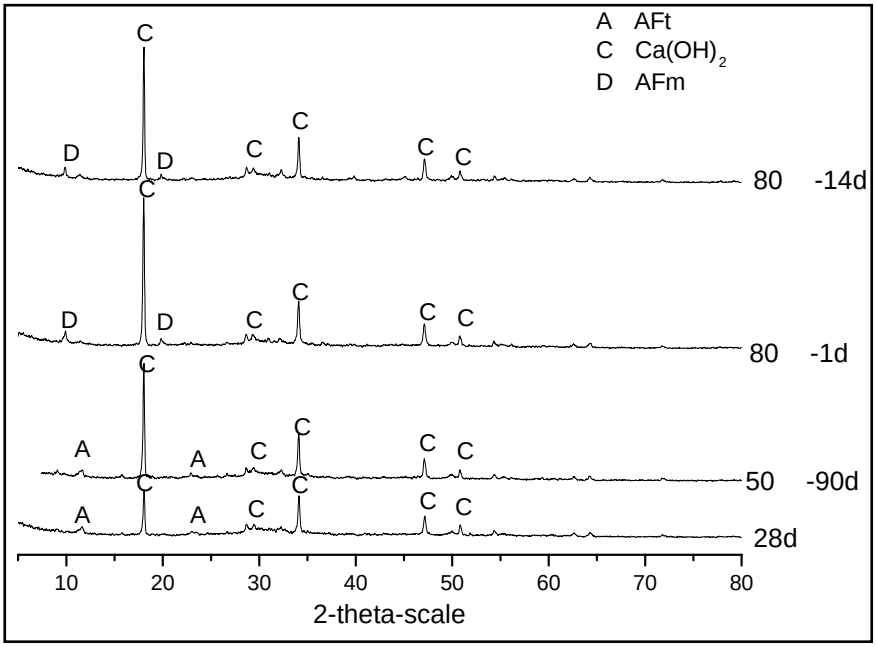

Figure 9. XRD pattern of hydration product in sample of ordinary Portland cement

Figure 10 is an XRD pattern of the hydration product of a sample with 50% ggbs, compared with the pattern for an ordinary Portland cement sample; the peak of $Ca(OH)_2$ is much lower than that for samples cured at standard condition and samples subjected to accelerated aging in hot water, which indicates that their $Ca(OH)_2$ content is less than the $Ca(OH)_2$ content in the hydration product of pure cement. With continuation of ageing in hot water, the peak of $Ca(OH)_2$ in hydration product of the sample with ggbs enhances also; however, the peak of $Ca(OH)_2$ for the sample aged for one day is higher than that aged for 14 days, which indicates that ggbs can absorb a small amount of $Ca(OH)_2$.

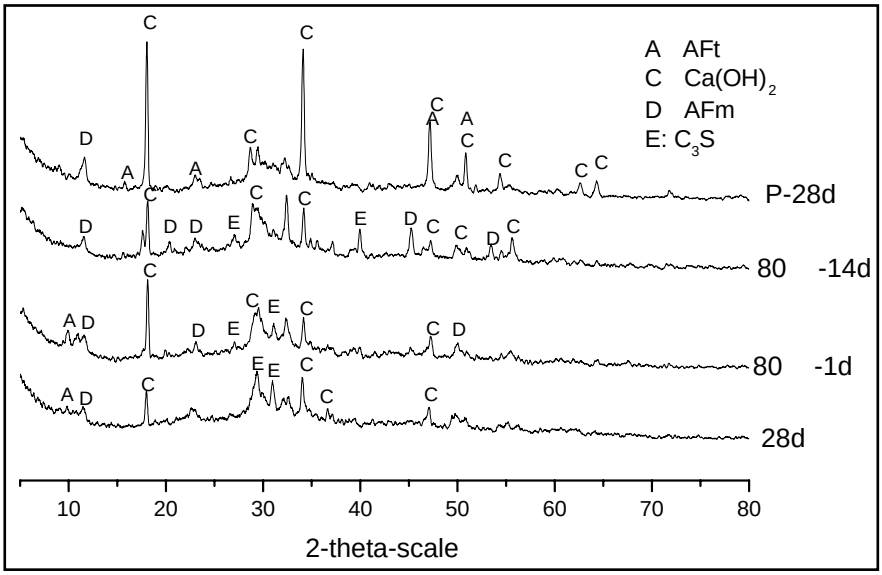

Figure 10. XRD pattern of hydration product in sample with 50% ggbs

Figure 11 is an XRD pattern of the hydration product of a sample with 20% microsilica. It can be seen from this pattern that its main products are AFt and CSH; there is no $Ca(OH)_2$ in either the sample cured at standard condition or the

sample aged in hot water. Moreover, with the passage of ageing time, the peak of CSH barely changes.

Figure 12 is an XRD pattern of the hydration product of the sample with 30% metakaolin. It is seen from the pattern that the main hydration products are AFt and $Ca(OH)_2$ as well as CSH; however, the $Ca(OH)_2$ content is relatively reduced before ageing. The peak of $Ca(OH)_2$ is sharper after the sample has been aged in 80℃ water for one day; however, the peak of $Ca(OH)_2$ is absent after the sample has been aged in 80℃ water for 14 days.

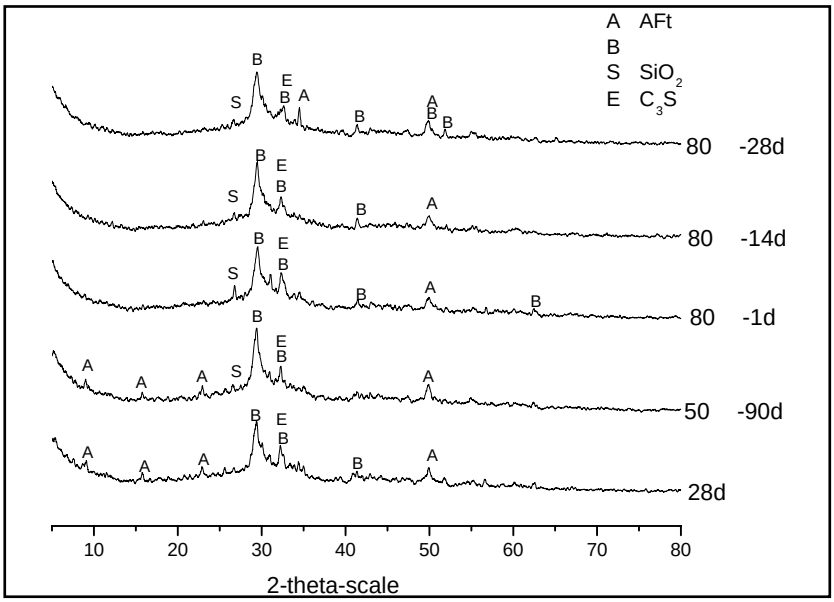

Figure 11. XRD pattern of hydration product in sample with 20% microsilica

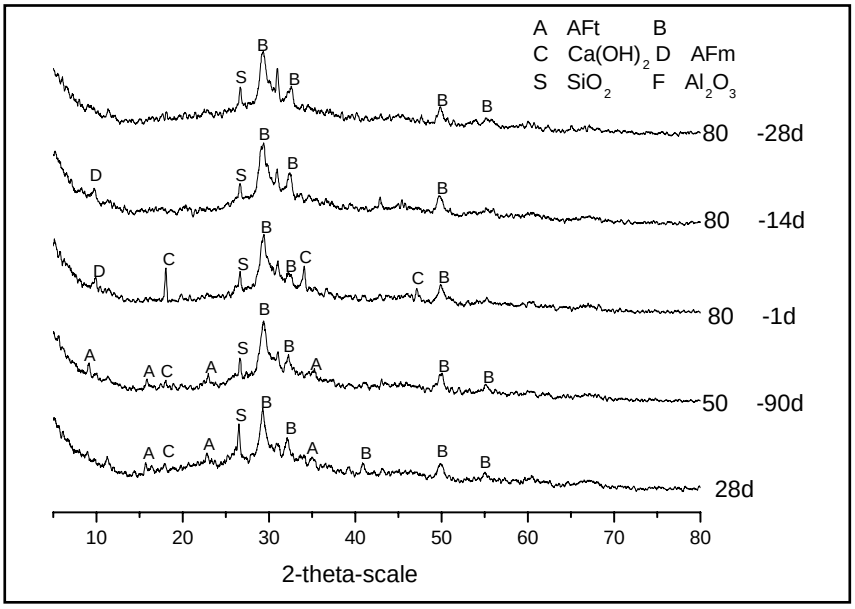

Figure 12. XRD pattern of hydration product in sample with 30% metakaolin

Figure 13 shows the XRD pattern of hydration product of a sample with microsilica and metakaolin. It can be seen from the pattern that its main product is AFt and CSH, and that the peak of $Ca(OH)_2$ is absent; samples were cured both at standard condition and aged in hot water.

It may be seen from the above XRD pattern that there is a large amount of $Ca(OH)_2$ crystals in the hydration product of ordinary Portland cement where samples were both cured at standard condition and aged in 50°C or 80°C water, but there is only a small amount of $Ca(OH)_2$ crystal in the sample with siliceous materials. It is thought that the main reason for this is: (1) cement content is reduced due to the addition of siliceous materials, which causes a reduction in $Ca(OH)_2$; (2) silicaceous material reacts with the hydration product of cement, which can absorb a part of. $Ca(OH)_2$.

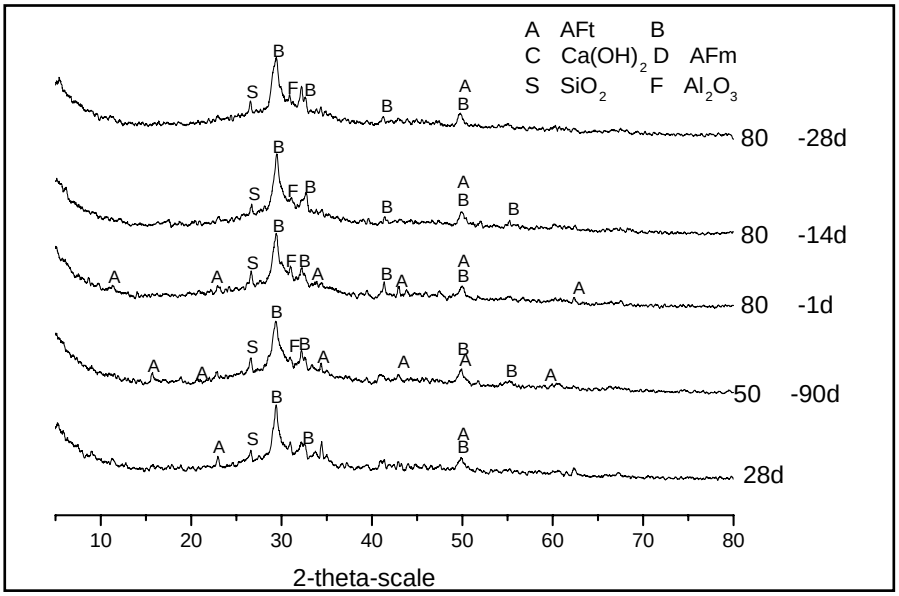

Figure 13. XRD pattern of hydration product in sample with microsilica and metakaolin.

It was found from the above pattern that there is hardly any $Ca(OH)_2$ in the hydration product of samples with microsilica, both for samples cured at standard condition and at accelerated ageing in 50°C or 80°C water; the peak of CSH is almost the same in several kinds of condition. The main reason for this is the high activity of microsilica, the microsilica having almost completely absorbed the $Ca(OH)_2$ at initial age.

4. Conclusions

By testing the mechanical properties and microscopic analysis of GRC samples with different silicaceous materials, the following conclusions can be drawn:

1. ggbs has little effect on improving GRC durability, even if ggbs content is up to 50%.
2. When using 20% metakaolin and 10% microsilica to replace cement, GRC durability was significantly improved.
3. When using 20% microsilica or 30% metakaolin to replace cement, GRC durability was improved to a certain extent.
4. Test results of mechanical properties are reported, observations of glassfibre outline and substance attached to glassfibre surface are described, together with the results of analysis of XRD peak of $Ca(OH)_2$ in hydration products.