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The influence of compound admixtures on the properties of high-content slag cement

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Abstract

Based on the activation theory of alkali and sulphate, the influence of compound admixtures on the properties of high-content slag cement was studied by testing the strength, pore structure, hydrates, and microstructure. Test results show that compound admixtures can obviously improve the properties of high-content slag cement.

Keywords: Fast-setting early strength agent; High-content slag cement; Compound admixture

1. Introduction

The cement industry is an important part of the national economy in our country. With the rapid increase of national economy and expansion of large scale construction, greater quality and quantity of cement is required. The development of the economy creates more wealth for human beings, but also consumes a large amount of resources and energy, causing environmental pollution that results in the destruction of the ecological balance. The production of Portland cement not only consumes limestone, clay, coal, and electricity, but also releases waste gases such as CO_2, SO_3, and NO_x, which can contribute to the greenhouse effect and acid rain.

In this paper, high-content blast furnace slag was studied. The aim is to increase the additive dosage to 70% or more, and decrease clinker dosage to 20% or less, as well as to ensure that the resulting cement possesses excellent physico-mechanical properties and good durability. In this way, we can better reach the goals of greatly saving natural resources and energy, reducing environmental pollution, and prolonging the service life of concrete buildings.

Slag cement is an important product in China; its output and usage scale is inferior to Portland cement, but its durability is better. According to Chinese state standard (GB1344-92), the amount of slag added in slag cement is allowed to be 20 to 70%. However, the strength of clinker produced in the shaft kilns extensively used in China is relatively low, with the result that the added amount of slag is often less than 40% for production of no. 425 slag cement. If the added amount of slag is increased, the early performance and the strength at 28 days may be affected. When the slag amount is greater than 70%, it is necessary to resolve the problems in early strength and setting time and to improve early performance and the strength at later stages.

The emphasis of the present research is two-fold: substituting gypsum with anhydrite and calcining gypsum. These both can improve early and later performance. There have been many reports on the influence of different gypsums on cement [1–4]. The related research work is extensive and has been a great benefit. It has been shown that if gypsum is replaced by other kinds of calcium sulphate in a similar condition, the added amount of slag may be increased by 15% without deteriorating the slag cement. Addition of alkali (such as alkali slag cement) is another effective method. There are many reports concerning alkali slag cement [5–8]. Of all alkali activations, water glass (liquid sodium silicate) is the most valid. Because water glass is a liquid, it is not suitable for production in a cement plant. Thus, it is necessary to use solid alkali admixtures such as Na_2SO_4 instead of water glass.

2. Results and discussion

2.1. Raw materials

Granulated blast furnace slag was from Nanjing 9424 steel plant, rotary kiln clinker was from Nanjing Qinlongshan cement plant, gypsum (G_1) was from Xuzhou, and an-

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Table 1
Chemical components of raw materials (wt%)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Total
Clinker	64.65	22.02	5.09	4.84	0.96	0.98	98.54
Slag	36.51	33.64	11.78	1.24	12.16		95.33
Gypsum	32.24		0.16			44.96	77.36
Anhydrite	36.02					51.45	87.47
Aluminium clay	0.21	33.36	46.93	1.18	0.17		81.85

hydrite (G_2) was from Nanjing gypsum ore. Na_2SO_4 (N) used was chemical material. A fast-setting early strength agent (F) containing $C_4A_3\overline{S}$ and $C_{11}A_7 \cdot CaF_2$ was made from limestone, aluminium clay (31.0%), gypsum (9.5%), and CaF_2 (0.5%) at about 1,250°C. The chemical components of the raw materials are shown in Table 1.

2.2. Compressive strength test

On the basis of activation of blast furnace slag (BFS), the added amount of slag is shown to be 70 and 90%. Table 2 shows test fills of slag cement with two-component admixtures. In Table 2, G1, G2, N, and F are gypsum, anhydrite, Na_2SO_4, and synthetic admixtures, respectively. The influences of these admixtures on mortar strength properties of slag cement are shown in Figs. 1, 2, and 3.

Fig. 1 shows that improvement was very obvious at early stage when using G2 and N admixtures, but the increase in strength at 28 days was less than that at early stages (compared with SG2 and SG3, SG4 and SG5).

Fig. 2 shows that enhancement of slag cement strength is very obvious not at early but at later stage, after increasing fineness from 300 to 450. For example, compared with SG1 (70% slag), the compressive strength of SG6 (70% slag) at 3, 7, and 28 days increased by 156.2, 69.6, and 18.7%. Even with SG8 (85% slag), the compressive strengths at early and later stages were all greater than SG1.

Fig. 3 shows the influence of G2 and F admixture on the strength of slag cement. Compared with SG1, the compressive strength of SG10 at 3, 7, and 28 days increased 8, 21, and 15.3 MPa, respectively. The increased production of ettringite at the early stage is a benefit to strength development, especially at 7 and 28 days.

Table 2
The test fills of slag cement with two-component admixture (wt%)

Number	Clinker	Slag	G1	G2	N	F	Fineness (m^2/kg)
SG1	25	70	5				350
SG2	25	70	5				300
SG3	23	70		5	2		300
SG4	15	80	5				300
SG5	13	80		5	2		300
SG6	23	70		5	2		450
SG7	13	80		5	2		450
SG8	8	85		5	2		450
SG9	22	70		4		4	375
SG10	19	70		5		6	375

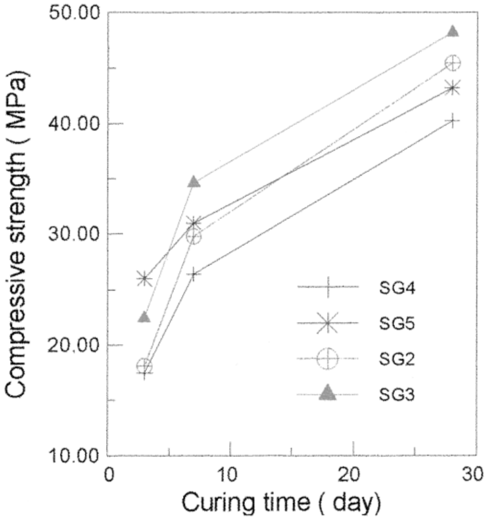

Fig. 1. Curing time vs. strength.

Table 3 shows the test fills of slag cement with three-component admixtures. The results of strength tests are shown in Figs. 4, 5, and 6. The purpose of the three-component admixtures is that based on mixing activate mechanism of NaOH-$Ca(OH)_2$-$CaSO_4$, the coordination between composite admixture and high slag cement must be considered. So with three-component admixtures, anhydrite and Na_2SO_4 were basic elements. The third element included alumstone (B), F1 (mainly containing $C_4A_3\overline{S}$ F3), (mainly containing $C_4A_3\overline{S}$ and $C_{11}A_7 \cdot CaF_2$). F3-1 was made of limestone, clay, gypsum, and CaF_2 and F3-2 was made of industrial by-products such as fly ash, phospho-gypsum, and so on. To allow comparison with anhydrite, calcined gypsum (G3) was adapted.

Fig. 4 shows the influence of different admixtures on the

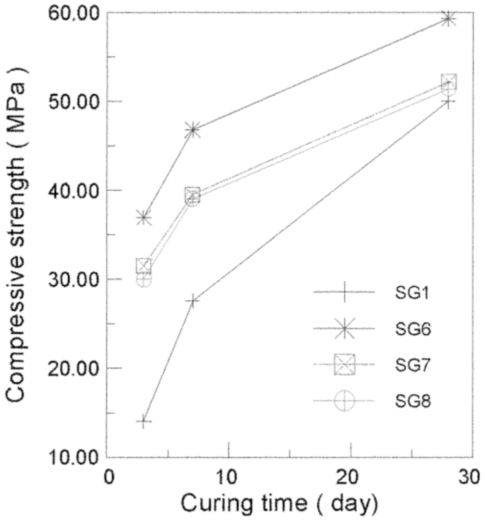

Fig. 2. Curing time vs. strength.

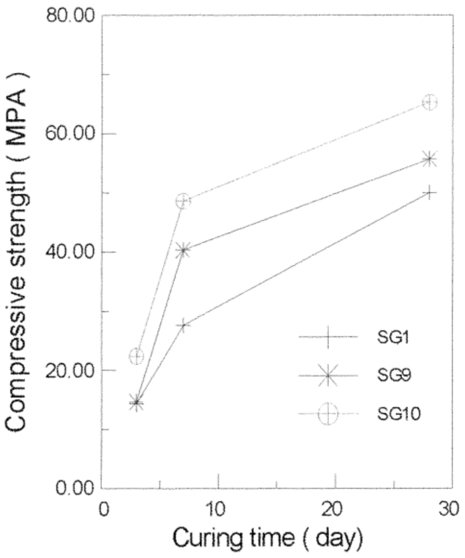

Fig. 3. Curing time vs. strength.

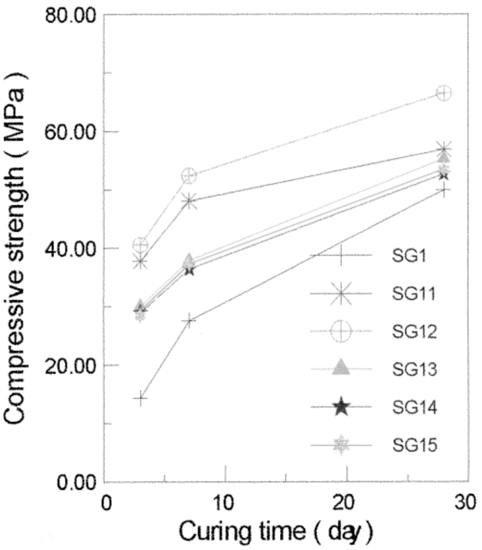

Fig. 4. Curing time vs. strength.

strength of high slag cement. Slag, clinker, and admixture content was 70%, 20%, and 10%, respectively. Reinforcing sequence of compressive strength was SG12 > SG11 > SG14 > SG13 > SG15. Compared with SG1, compressive strength of SG12 at 3, 7, and 28 days increased 24.2, 24.8, and 16.6 MPa.

Fig. 5 shows the influence of different Na_2SO_4 content on the strength. Test results show that although the reinforcing effect of early compressive strength of SG19 was not very obvious, the strength at 28 days was the highest. It had reached the no. 625 standard. From test results, it is well known that added alkali content should be suitable to slag content. Fig. 6 shows the influence of admixture element, content, slag content, and cement fineness on the strength of slag cement. Results show that provided rationally three-component admixtures were adapted, both early and later strengths were enhanced. For example, when slag content was 90%, the compressive strength at 28 days can reach no. 425 slag cement standard, although early strength was lower.

2.3. Pore structure test

Three mortar cement samples were chosen: SG1 (common slag cement of 70% slag), SG12 (slag cement of added admixture of 70% slag), and SG20 (slag cement of added admixture of 80% slag). Pore structure was tested by auto-60 porosimeter (Quantachrome, Boynton Beach, FL, USA).

Fig. 7 shows the relation between hydration time and total porosity. Compared with SG1, at hydration early stage (1 day), the total porosity of SG12 decreased to 20.64% from 22.90%. At 28 days of hydration, the total porosity decreased to 12.92% from 16.02%.

Fig. 8 shows the influence of hydration time on pore distribution. Compared with SG1, at 1 day of hydration the pore ratio of less than 50 nm of SG12 increased to 42.92% from 31.34%. On the contrary, pore ratios of more than 100 nm of SG12 decreased to 40.26% from 59.83%. At 28 days of hydration, pore ratios of less than 50 nm of SG12 increased to 92.32% from 89.6%. The pore ratios of more than 100 nm of SG12 decreased to zero from 7.06%. It is

Table 3
The test fills of slag cement with three-component admixtures (wt%)

Number	Clinker	Slag	G2F3-1N	G3F3-1N	G2F1N	G2F3-2N	G2BN	Fineness (m^2/kg)
SG11	20	70		4/4/2				375
SG12	20	70			4/4/2			375
SG13	20	70					4/4/2	375
SG14	20	70	4/4/2					375
SG15	20	70				4/4/2		375
SG16	18	70	5/6/1					375
SG17	17	70	5/6/2					375
SG18	17	70	4/6/3					375
SG19	21.5	70	4/3/1.5					375
SG20	10	80	4/4/2					450
SG21	5	85	4/4/2					450
SG22	2	90	4/4/2					450

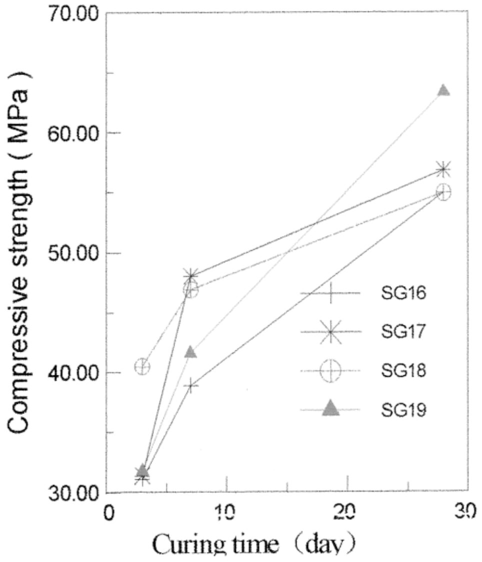

Fig. 5. Curing time vs. strength.

shown that composite admixture improved the pore structure of high-content slag cement.

2.4. Hydration mechanism

From the above strength and pore structure tests, it can be seen that according to the hydration mechanism of alkali-activated slag cement and Portland slag cement, the mixed activation mechanism of sodium-calcium-sulfate was promoted forward. At the same time, by using quick hardening and super early strength cement, admixtures containing $C_4A_3\overline{S}$ and/or $C_{11}A_7 \cdot CaF_2$ were synthesized. It played an important part in ettringite formation in early stages and in the enhancement of strength. With this background, compound admixtures with three components have been devel-

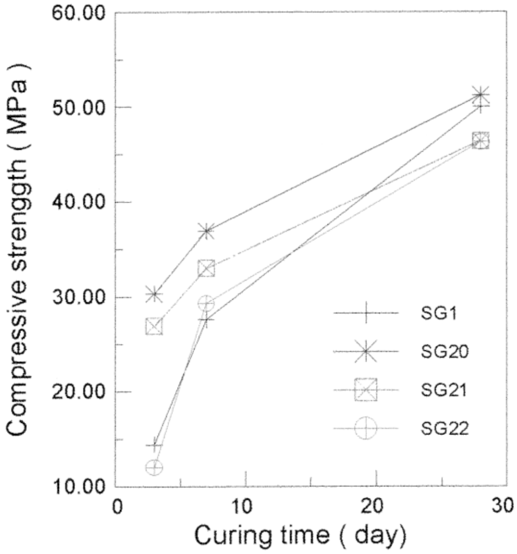

Fig. 6. Curing time vs. strength.

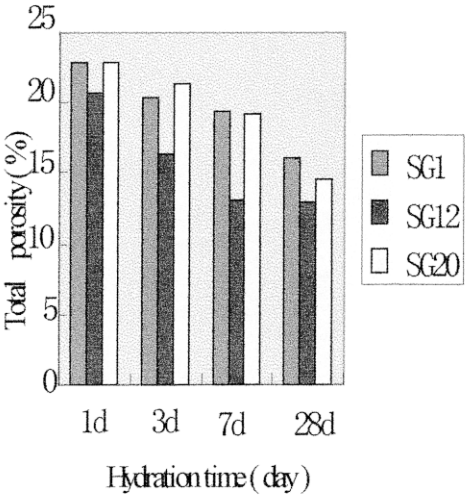

Fig. 7. The influence of hydration time.

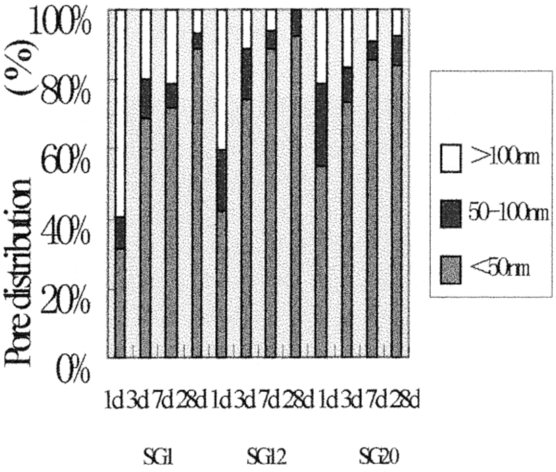

Fig. 8. The influence of hydration time on porosity of slag cement.

Table 4
Polymerization degree of hydration products of slag cement

Number	Uni-poly (%)	Bi-poly (%)	Tri-chain (%)	Tetra-circle (%)	High-poly (%)
SG1					
1 day	13.78	7.87	1.40	1.27	2.98
3 days	11.39	6.38	1.90	0.73	3.52
7 days	11.29	6.47	2.08	0.44	3.93
28 days	8.93	5.03	2.53	0.82	4.54
SG12					
1 day	13.80	7.31	1.93	0.86	3.24
3 days	13.39	8.21	2.63	0.66	3.96
7 days	12.19	6.96	3.16	0.54	4.63
28 days	7.85	5.53	3.64	0.93	5.51
SG18					
1 day	12.41	6.52	1.86	0.36	3.01
3 days	12.25	6.06	2.42	0.39	3.73
7 days	10.95	5.88	3.52	0.84	4.52
28 days	7.95	5.25	3.87	1.01	5.45

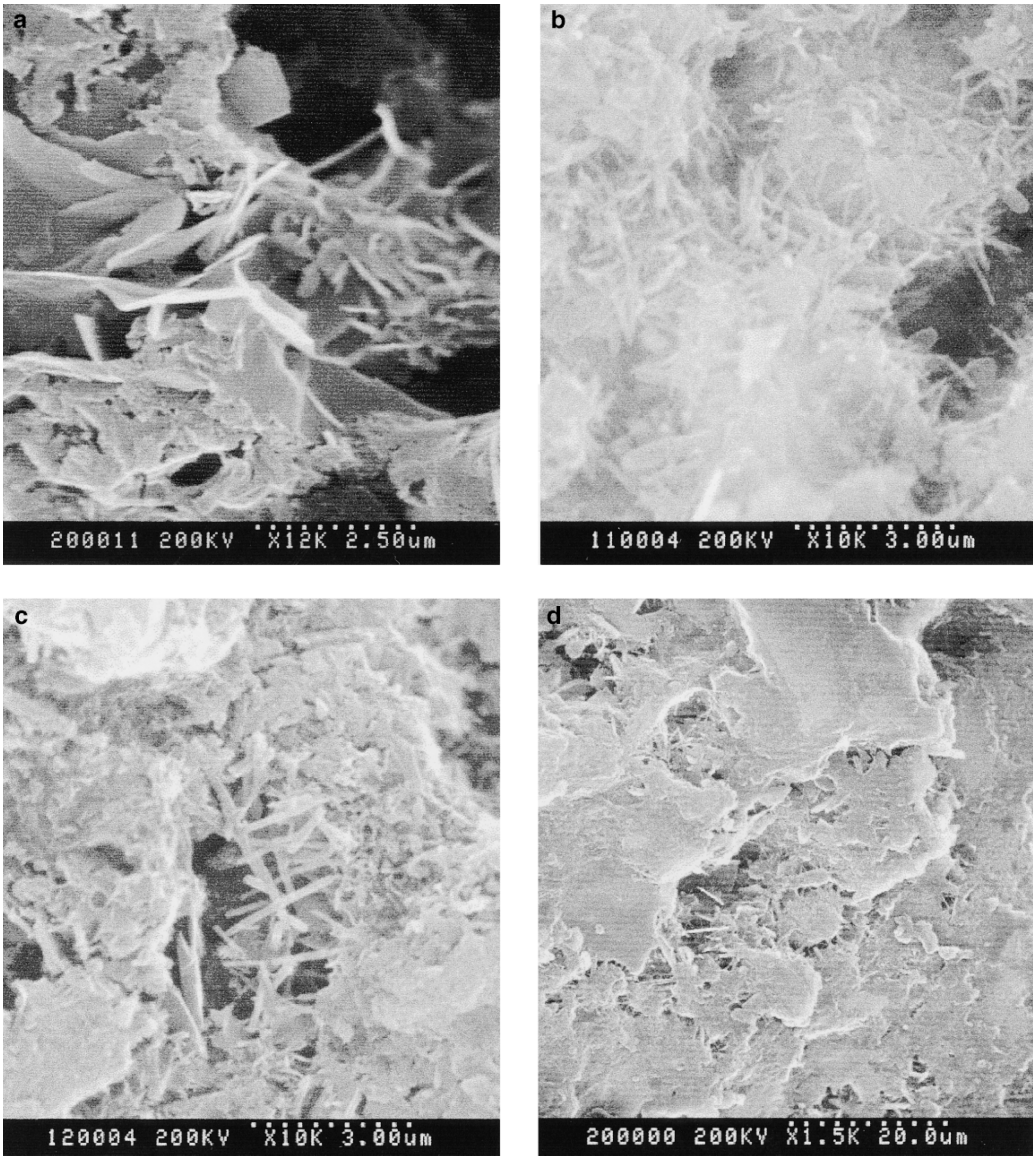

Fig. 9. Scanning electron microscopy photo of high-content slag SG18 at different ages. (a) Pore distribution at 7 h of hydration (SG18); (b) at 12 h of hydration (SG18); (c) at 1 day of hydration (SG18); and (d) at 90 days of hydration (SG18).

oped that substantially improved the strength and pore structure at early and later periods. Improvement of these properties can be explained by the analysis of hydration products and polymerization degree measurement of silicate anion.

Table 4 shows the test results of polymerization degree of hydration products of slag cement (SG1, SG12, SG18) at 1, 3, 7, and 28 days of hydration. The polymerization degree of hydration products was tested by using the trimethysily technique (blended solvent methods and Lentz methods) in association with gas-liquid chromatography and gel-permeation chromatography. Table 4 shows that with the continuation of hydration, the uni-poly and bi-poly ratio decreased, and chain-poly and high-poly ratios increased. At early stages of hydration, the variation of uni-poly and bi-poly ratio was not obvious, but there was greater change at 28 days of hydration. This can be explained as follows: At early stages of hydration, although polymerization of hydration products made uni-poly and bi-poly ratio decrease, the breakage of slag made uni-poly and bi-poly ratio increase. Thus, these two actions offset each other. At later stages of hydration, the polymerization of hydration played an important part; thus, the high-poly ratios increased. Compared with SG1, at early stages (1–7 days), uni-poly and high-poly ratio of SG12 and SG18 all increased. This shows the breakage rate of slag and the polymerization rate of hydration products. This is due to the action of compound admixtures.

Fig. 9 shows the microstructure of hydration products at different ages. At 7 h of hydration (Fig. 9a), due to fast hydration of early strength ore, the dissolution rate of gypsum was lower, so there was AFm evident in scanning electron microscopy. At 12 h of hydration, because of the continuing dissolution of gypsum, breakage of slag and dissolution of anion are very beneficial to production of ettringite. Needle ettringite can be clearly seen in Fig. 9b. At 1 day of hydration, ettringite was in the stages of separation and advancement, so bar ettringite can been seen in Fig. 9c. It played the action of advancing skeleton and microsteel fiber. Connecting and filling between the ettringite and C-S-H gel have important influences on improvement of the early stage functioning and dense structure formation. At 90 days of hydration, much of the ettringite was wrapped in C-S-H gel and coated by slag particles. It is shown that the hydration of slag surface was greater. More and more C-S-H filled into the pore of hardened paste, so that the later properties could be improved.

3. Conclusions

1. Two-component admixtures lead to better action on slag cement, but early and later properties cannot be considered at the same time.
2. To obtain high strength slag cement, it is necessary to use three-component admixtures in high-content slag cement.
3. Compound admixtures not only speed up the breakage of slag structure, but also accelerate the hydration of clinker and the solution of anhydrite and lead to production of more hydrates and improvement in all properties of high-content slag cement. This was verified by scanning electron microscopy, pore structure analysis, and polymerization degree measurements of silicate anion.

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