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Improvement of Strength and Chemical Resistance of Silicate Polymer Concrete

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Abstract: It has been known that acid-resistant concretes on the liquid glass basis have high porosity (up to 18~20%), low strength and insufficient water resistance. Therefore they can not be used as materials for load-bearing structural elements. Significant increasing of silicate matrix strength and density was carried out by incorporation of special liquid organic alkali-soluble silicate additives, which block of superficial pores and reduces concrete shrinkage deformation. It was demonstrated that introduction of tetrafurfuryloxisilane additive sharply increases strength, durability and shock resistance of silicate polymer concrete in aggressive media. This effect is attributable to hardening of contacts between silicate binder gel globes and modification of alkaline component owing to "inoculation" of the furan radical. The optimal concrete composition with the increased strength, chemical resistance in the aggressive environments, density and crack resistance was obtained.

Keywords : silicate polymer concrete, additives, tetrafurfuryloxisilane, furfuryl alcohol.

1. Introduction

It is well known that silicate polymer concrete (SPC) consists of a binder, a hardener, a polymeric additive, filler and an aggregate. Water-soluble sodium silicate or potassium glass with density $(1.38\sim1.4)10^{-3}$ g/mm^3 applies as a binder. Technical sodium silicofluoride is used in most cases as a hardener. Fillers and aggregates are natural or artificial materials with acid resistance no less 90%, in particular: diabases, basalts, granites, andesites etc. Silicate polymers can be prepared in the form of mastics, solutions or concrete depending on grain size distribution. SPC has a lot of the important consumer properties: high density, fire resistance, durability and acid resistance. However these concretes have the grave practical disadvantages: small application life and large shrinkage deformation.

Improvement of SPC structure can be obtained by introduction of the acid resistance or inert to silica gel polymeric additives chemical interacting with water .These additives must be well combined with liquid glass and hardened by acids . The polymeric materials applied to updating of SPC can be different both by the nature and the mechanism of their influence as example: densifying or dispersing agents (furan, phenolic and other resins), water reducing agents (compounds with N-C-O groups etc.), shrinkage reducing agents (oligoesters), slowing down of hardening agents (sulphanole, organo silicon liquids) and clogging agents (rosin, sulfur etc.). Introduction furfuryl alcohol (FA), tetrafurfuryloxisilane (TFS) or some other oligomers in structure of SPC does these concrete an aggressive environment tight.

Optimal composition of SPC can be produced from conditions of the minimal content of the binder, good workability and high density of concrete.

2. Optimal composition of silicate polymer concrete

2.1 Influence of the liquid glass and the monomeric additive content on the SPC fluidity, harshness, workability and strength

It is apparent that strength of SPC as a structural material depends on a ratio: binder-aggregate at conservation of technological plasticity of a mix. We investigated influence of the liquid glass and the monomeric additive content on fluidity and harshness of the SPC mixes. Results of the experiments are presented in Table 1.

One can see that small change of liquid glass quantity changes drastically the technical characteristics of SPC mixes. Reduction of binder quantity by 15% reduces fluidity of the mix in 2, 5 times and almost in 5 times increases its harshness.

Influence of the monomeric additive (TFS) on technological properties of SPC was investigated with plastic mix (content of liquid glass is 11%). Experimental results are illustrated in Table 2.

Results of the research show, that introduction of TFS increases harshness of SPC mixes.

As regards workability of the investigated compositions it can be said that for content of the liquid glass (11%) and the monomeric additive (3%), the SPC mix can be classified as "plastic".

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Table 1 Influence of the liquid glass content on fluidity and harshness of SPC mixes.

Content of the liquid glass (%)	Fluidity of the SPC (mm)	Harshness of the SPC mix (sec)	Kind of the SPC mix
13	150	5	High workability concrete
12	120	10	
11	60	23	Plastic concrete
10	0	30	Dry mix concrete

Table 2 Influence of the TFS additive on fluidity and harshness of SPC mixes.

TFS additive content of liquid glass (%)	Fluidity of the SPC mix (mm)	Harshness of the SPC mix (sec)
Without additive	60	23
2	40	24
3	20	28
6	0	32

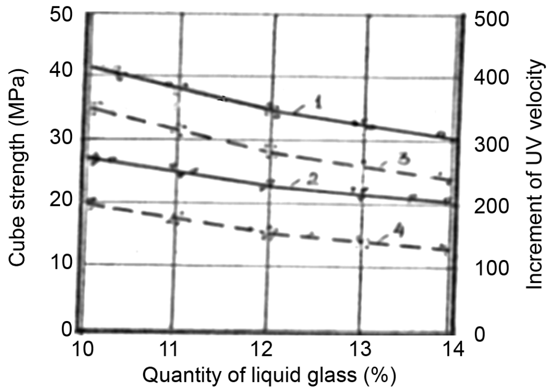

Fig. 1 Change of strength and density of SPC depending on the consumption of the liquid glass: 1-Change of SPC strength with the TFS additive, 2-Same without the additive, 3-Change of US velocity into SPC mix with the TFS additive, 4-Same without the additive.

Influence of quantity of liquid glass on SPC strength was defined both for compositions with the monomeric additive and without it.

Investigated SPC compositions are shown in Table 3. Results of experiments are shown in Fig. 1 and Table 4.

One can recognize that strength and density of SPC compositions will increase with reduction of the liquid glass content in all range of its change. So decrease of the liquid glass content by 3% (mixes 1, 4 and 5, 8) leads to increase in SPC strength approximately by 25%. It should be emphasized that introduction into SPC composition 0.3% TFS increases strength and density of the material approximately by 50% in all range of the liquid glass consumption. It is believed that increase of strength and density of SPC mix with reduced content of the liquid glass is connected with thickness of a binder film which envelops of the filler's large grains. As this takes place the thinner film the better its adhesive bond ability properties and, hence are better strength of a concrete as a whole.

2.2 Optimization of SPC composition

Application plastic SCP mixes allows to produce structures with any configurations and conditions of a concrete placement. Because of this optimization of SPC composition was made provided that the quantity of liquid glass will be within the limits of 11~11.5% and 3% of the monomeric additives FA or TFS (from weight of the liquid glass).

For optimization of SPC composition influence of three factors was studied:

- x_1 - Weight ratio of liquid glass to filler ;
- x_2 - Content of sand in a mix of fillers ;
- x_3 - Content of liquid glass in a mix.

Effectiveness functions were compressive strength in the SPC mix age of 28 day $\hat{Y}_{st}$ and harshness of the SPC mix $\hat{Y}_{hr}$ with the provision that harshness is not more 30 sec.

The following regression equations were obtained:

$$\hat{Y}_{st} = 37.6 - 5.7x_1 - 1.5x_2 + 17x_1x_3 \quad (1)$$

$$\hat{Y}_{hr} = 23 - 4.5x_1 - 15x_3 + 7.4x_1^2 + 4.4x_2^2 \quad (2)$$

by means of which the optimized composition of SPC was found (Table 5).

The physical-mechanical properties of the optimum SPC com-

Table 5 Optimal composition of SPC.

No. composition	1	2	3
Components	Content (% of mass)		
Liquid glass (1.4×10^{-3} g/mm^3)	11.23	11.23	11.23
$3Na_2SiF_6$ (2.7×10^5 mm^2/g)	1.68	1.68	1.68
Diabase flour (2.4×10^5mm^2/g)	20.06	20.06	20.06
Quartz sand	26.71	26.71	26.71
Granite chippings (5~10 mm)	40.32	30.98	30.98
FA	-	0.34	-
TFS	-	-	0.34
Total	100	100	100

Table 3 Composition of SPC mixes.

No. composition	1	2	3	4	5	6	7	8
Content	Content (% of mass)							
Liquid glass	10	11	12	13	10	11	12	13
Na_2SiO_6	1.5	1.7	1.8	2.0	1.5	1.7	1.8	2.0
Diabase flour	18	18	18	18	18	18	18	18
Quartz sand	28	28	28	28	28	28	28	28
Granite chippings	42.5	41.3	40.2	39	42.2	40.97	39.84	38.61
TFS	-	-	-	-	0.3	0.33	0.36	0.39

Table 4 Influence of the liquid glass content on strength of SPC compositions.

No. composition	1	2	3	4	5	6	7	8
Ultimate compression strength (MPa)	27	25.8	23.7	21.7	40.1	38	35.4	32.4

positions are illustrated in Table 6. It should be noted that SPC mix modified by TFS has higher strength indexes and greater deformability. Study of shrinkable deformations has shown, that introduction of monomeric additives leads to significant reduction shrinkage. 3% of TFS (from weight of liquid glass) reduces of shrinkable deformations up to 0.06%. The greater shrinkage of SPC mix without the additive take place in the first day (up to 70%) then it goes slowly and stops for 32~35 days (Fig. 2).

SPC mix with the monomeric additives is characterized by exponential increasing of shrinkage deformations. Formation of SPC structure is accompanied by intensive compression of liquid glass gel by capillary forces of intermicellar liquid. The compression of the gel causes maximal shrinkage deformation from the very beginning of hardening. Introduction of FA or TFS considerably reduces influence of capillary forces owing decreasing of liquid tension into capillaries.[1,3]

3. Chemical resistance and durability of silicate polymer concrete

It is known that an elevated permeability of usual SPC based on liquid glass is intimately connected with the big porosity and filtering defects. Because of this application of commonly used SPC requires leak proof and chemically stable lining from expensive materials (lead, polyisobutylene etc.). We investigated filtrational and diffusive permeability of SPC with monomeric additives (TFS, FA) in aggressive environments

3.1 Filtration permeability

For studying of filtration permeability the compositions of SPC samples were accepted in accordance with optimal composition given in Table 5. Water was used as a filtrational liquid because it did not influence on consolidation of the concrete. It has allowed to judge about presence or absence of filtering defects in investigated compositions and to estimate influence of additives on filtrational permeability. Obvious that for SPC compositions bearing the tests by water, a filtration of acids will be absent, as the effect of consolidation of the material in this case is shown.

Hydrostatic pressure was accepted equal 0.3~0.4 MPa. This value corresponded to application of SPC as a structural material in pressure tanks, bottoms evaporative surface condensers, storage of acids pickling baths etc. Maximal overflow pressure was equaled 0.6 MPa. The greatest pressure at which water did not leak out through SPC samples and "sweating" of this samples did not observed was accepted as a degree of waterproofing of the composition. Results of the test are presented in the Table 7.

Obtained data show that all SPC samples with monomeric additives withstand the pressure of water 0.6 MPa, whereas samples without the additive (composition 1) started a leakage after 1~1.5 hours of test at overflow pressure 0.1 MPa. Thus it is obvious that additives TFS and FA eliminate the filtering defects in the form of microcracks and conducting channels on a border "gel-filler."

3.2 Diffusive penetration

The durability of SPC structures under aggressive environments depends on diffusion rate of chemically active reagents into a material. Fluid penetration is realized through imperfections in molecular packing of the binder and it is accelerated at increasing of temperature and pressure. In this connection definition of diffusion coefficient (as a key parameter of a liquid carryover) becomes the important problem.

It has been known that big number of aggressive liquids is used in the form of water solutions and thus studying of water diffusion in SPC is important. We investigated diffusive penetration of SPC in the neutral water environment which is the most aggressive reagent for liquid glass compositions. With knowledge of value diffusion coefficient for time frame it is possible to estimate influence of the monomeric additive and to establish maximum allowable concentration of an aggressive environment. Results of tests of compositions 2 and 3 is illustrated in Fig. 3.

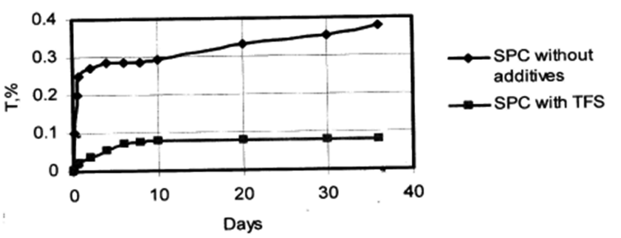

Fig. 2 Change of shrinkable deformations T (%) during hardening of SPC.

Table 7 Filtration permeability of the SPC compositions.

No. composition	Permeability at pressure (MPa)
1	0.1
2	0.6
3	0.6

Table 6 Physical-mechanical properties of optimal SPC compositions.

Index	Unit	No. optimal composition		
		1	2	3
Cube strength	MPa	20~25	28	36~41
Prism strength	MPa		20~22	30~35
Tensile strength	MPa	1.5	3.2	4.1
Tensile strength at bend	MPa		6	10
Elasticity modulus	MPa	$(1.6\sim1.7)10^{4}$	$(1.9\sim2.1)10^{4}$	$(2.4\sim2.6)10^{4}$
Poisson coefficient			0.23	0.21
Longitudinal strain	mm/m		$(140\sim150)10^{-5}$	$(150\sim165)10^{-5}$
Transverse strain	mm/m		$(30\sim40)10^{-5}$	$(55\sim60)10^{-5}$
Toughness	kJ/m^2		2.3	5.4
Coefficient of thermal expansion	$1/^{o}C$		8×10^{-6}	8.7×10^{-6}
Shrinkage at hardening (after 28 days)	%	0.39	0.22	0.06

It can be seen that process of diffusive penetration of SPC compositions modified by FA after 25 day, remains practically constant unlike the composition 2 modified by TFS. The diffusive coefficients obtained by a sorption method were calculated for two periods activity of the water media: 7 and 30 day. Results of the calculation are given in the Table 8.

Therefore introduction modifiers from furan row in SPC composition allows to reduce the speed of liquid transfer velocity.

3.3 Influence of monomeric additives on chemical resistance of SPC compositions

Corrosion stability of SPC in high concentration acid media permits the use it widely in anticorrosive techniques . However, corrosion resistance of SPC in alkalis and in weak water solutions of acids is not enough. The effect of corrosion in such environments is shown in deposition of salts in pores, cracks and other voids. Crystallization of these salt depositions introduced by the corrosion environment or formed by chemical reaction of the material and environment leads to destruction of a silicate composition.

High diffusive penetration of SPC can be drastically lowered by the active additives capable to raise SPC density and therefore its corrosion resistance. As indicate above the most effective results were obtained at introduction of FA or TFS additives. Addition of monomeric additives to silicate composition improves the physical-mechanical characteristics and chemical resistance of silicate compositions due to improvement in the quality of silicate bonds and better adhesion between the binder and coarse filler[2]. In the other words influence of the monomeric additives is conditioned by consolidation of liquid glass gel during it hardening and modifications of alkaline components due to "inoculation" of furan radical.

Consolidation mechanism of SPC composition containing these additives can be considered as resulted from two processes: decompression of silicon acid gel due to decrease in the surface tension of intermicellar liquid and polymerization under the influence of acid solutions.

Considering FA and TFS as consolidation additives, it should be noted that penetration of the SPC compositions modified by FA strongly depends on concentration of an aggressive environment.

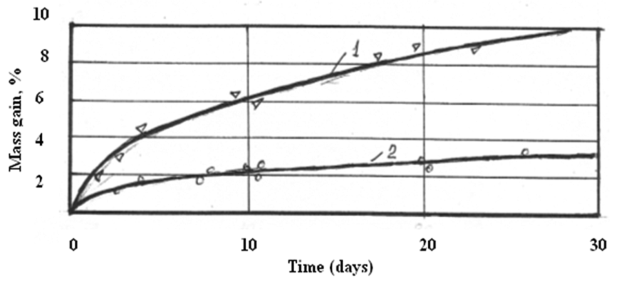

Fig. 3 Change of weight of SPC samples in water: 1-composition modified by FA; 2-same but by TFS.

Table 8 Diffusive coefficients water in SPC compositions.

No. composition	Diffusion coefficient 10^{-5} (mm^2/sec)	
	After 7 days	After 30 days
2	8.77	8.91
3	0.74	0.25

Polymerization rate of FA in the silicate media under the action of aggressive environments depends on pH especially on the first reaction stages. Corrosion of silica by hydrofluoric acid occurs rather quickly and leads to loosening of SPC composition and increasing of diffusive penetration. Because of this application of the consolidation additive FA is desirable at pH ≤ 5

The mechanism of TFS action as consolidation additive in these environments is a little other: there is a hydrolysis of TFS with formation of an orthosilicic acid and FA.[3] Inorganic cement fills the saddles between globules of silica gel. Increasing of the contact area leads to significant growth of durability and by doing so compensates strength reduction due to etching a matrix by hydrofluoric acid. In that way TFS essentially reduces the diffusive penetration of water and faintly acids and allows to use SPC for reinforced structures without special protection of a reinforcement.

3.4 Chemical resistance of SPC in faintly acid environment

The studying of the SPC penetration in faintly acid environment has performed for optimal composition including consolidation monomeric additives FA or TFS (Table 5). Concentration of aggressive environments corresponded to sulfuric and hydrochloric acids solutions applied for pickling of metals. Corrosion stability of SPC was estimated by change of compression strength of the SPC samples during 3~18 months exposition in the environment with 3 months interval. Corrosion resistance coefficients of SPC compositions including FA and TFS additives are given in Table 9.

The experimental data allowed to obtain the analytical interrelationship of *chemical stability coefficients* of the SPC compositions modified by TFS and FA additives in hydrochloric acid : $K_{(HCl., FA)}$, $K_{(HCl., TFS)}$ and sulfuric acid: $K_{(H_2SO_4, FA)}$, $K_{(H_2SO_4, TFS)}$ environments and their concentration and time of an exposition

$$K_{(HCl., FA)} = 0.99 + 2.19 \times 10^{-3} C - 4.36 \times 10^{-3} \tau + 5.07 \times 10^{-4} C\tau \quad (3)$$

$$K_{(H_2SO_4, FA)} = 0.95 + 8.03 \times 10^{-3} C - 0.13 \times 10^{-} \tau + 1.1 \times 10^{-4} C\tau \quad (3a)$$

$$K_{(HCl., TFS)} = 0.91 + 7.37 \times 10^{-3} C - 3.62 \times 10^{-3} \tau + 2.86 \times 10^{-4} C\tau \quad (4)$$

$$K_{(H_2SO_4, TFS)} = 0.93 + 4.21 \times 10^{-3} C - 2.6 \times 10^{-3} \tau + 6.1 \times 10^{-4} C\tau \quad (4a)$$

where C - solution strength (%) , τ- time of exposition (months)

By taking $K \geq 0.8$ can forecast the SPC composition service life in the aggressive acid environment of various concentration.

Influence of a kind of the monomeric additives on SPC corrosion stability is resulted in the Table 10.

4. Conclusion

1) Small change of liquid glass quantity changes drastically the technical characteristics of SPC mixes.

2) Introduction of TFS increases harshness of SPC mixes.

3) Strength and density of SPC compositions will increase with

Table 9 Corrosion resistance coefficients of SPC compositions.

Concentration of acid (%)	Time of exposition (months)	SPC with TFS		SPC with FA	
		H_2SO_4	HCl	H_2SO_4	HCl
1	3	0.97	0.92	0.96	0.89
2		0.99	0.97	0.89	0.98
5		1.00	0.98	0.93	0.97
10		1.02	1.03	0.97	0.98
20		1.04	1.06	1.02	1.03
1	6	0.96	0.94	0.88	0.90
2		0.97	1.01	0.91	0.94
5		1.01	1.03	0.92	0.96
10		1.05	1.05	1.01	1.03
20		1.08	1.11	1.10	1.05
1	12	0.93	0.88	0.91	0.97
2		0.96	0.96	0.90	0.91
5		1.03	1.02	0.90	1.01
10		1.06	1.07	0.98	1.04
20		1.12	1.17	1.08	1.08
1	18	0.89	0.86	0.83	0.85
2		0.92	1.03	0.87	0.88
5		1.02	1.04	0.91	1.03
10		1.05	1.06	1.02	1.05
20		1.12	1.10	1.07	1.06

Table 10 Ultimate compressive strength of SPC versus kind of the additive and the corrosion environment.

Kind of additive	Aggressive media		
	Absence	2% H_2SO_4	2% HCl
TFS	33.8	36.3	34.6
FS	25.3	25.0	24.8

reduction of the liquid glass content.

4) Optimal composition of SPC includes 11.23% of liquid glass and 0.34% monomeric additives (FA or TFS).

5) SPC mix modified by TFS has higher strength indexes (cube strength up to 41 MPa) and (that is especially important) greater deformability.

6) Introduction of monomeric additives leads to significant reduction shrinkage. 3% of TFS (from weight of liquid glass) reduces of shrinkable deformations up to 0.06%.

7) SPC samples with monomeric additives withstand the pressure of water 0.6 MPa. Additives TFS and TA liquidate the filtering defects in the form of microcracks and conducting channels on a border "gel-filler."

8) Introduction of modifiers from furan row in SPC composition allows to lower speed of liquid transfer velocity.

9) Corrosion of silica by hydrofluoric acid occurs rather quickly and leads to loosening of SPC composition and increasing of diffusive penetration Because of this application of the consolidating additive FA is desirable at pH ≤ 5.

10) Chemical stability coefficients of the SPC compositions modified by TFS and FA additives exposed in acid environments are obtained.

11) Influence of a kind of the monomeric additives on SPC corrosion stability is revealed.

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