Pergamon

Cement and Concrete Research, Vol. 28, No. 1, pp. 13–18, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(97)00192-0

SILICA FUME–SODIUM HYDROXIDE BINDING SYSTEMS

A. Bajza,* I. Rouseková,* and V. Živica[1]†
*Faculty of Civil Engineering, Slovak Technical University, Radlinského 11, 813 68 Bratislava, Slovak Republic
†Institute of Construction and Architecture, Slovak Academy of Sciences, Dúbravská cesta 9, 842 20 Bratislava, Slovak Republic

(Received July 1, 1997; in final form September 8, 1997)

ABSTRACT

This paper describes the utilization of alkali-silica reaction as a hardening and strengthening process. It is shown that, at an optimum composition, a binder based on silica fume and sodium hydroxide can produce composites having compressive strength comparable to the values of Portland cement-based materials. However, the composites based on the above-mentioned alkali-silica binder are not hydraulic. The hydraulicity of the binder is a task for further study. *© 1998 Elsevier Science Ltd*

Introduction

In concrete technology the following alkali-silica reactions are of interest: 1) The reaction of alkalies that are present in cement (with a content over 0.9%) with reactive amorphous silica or poorly crystallized quartz (opal, chalcedony) present in an amount of about 5% of some aggregates (1,2). This reaction can result in expansion and cracking of concrete. It represents a destructive process. 2) The reaction between alkalies in water glass and finely ground siliceous material (quartz, andesite, diabase, etc.) in the presence of Na_2SiF_6; this represents a positive binding process used in the production of a special acid-resisting concrete (3,4). 3) The reaction between alkalies in carbonates, hydroxides, or silicates and basic blast furnace slag, known as alkali activation; this is used in the production of slag-alkali concretes (5,6).

All above-mentioned alkali-silica reactions are based on the reaction of amorphous or glassy SiO_2 and alkalies, and result in the formation of alkali silicate hydrates. Their effect on the properties of the produced composite is significantly dependent on its physical state: it is destructive in the case of hardened composite (Reaction 1) but nondestructive in the case in which the system is in fresh and plastic state (Reactions 2 and 3). Experience shows that it is possible to use the alkali-silica reaction (ASR) for production of high-quality composites in both of the latter cases.

At present, alkali activation is not successfully developed and utilized. The main direction of its application tends toward slag-alkali concretes. We believe that more attention should

---

Communicated by J.P. Skalny.

[1] To whom correspondence should be addressed.

be paid to the alkali activation of slag as well as to using alkali activators themselves as binding systems. Existing industrial wastes contain active alumina and silica components, which are a convenient base for the utilization of certain technologies. Systems capable of working in the absence of Portland cement are of great interest and are expected to have applications in the future; thus, their investigation is desirable.

The above knowledge was the motivation for our research. We have chosen silica fume as the active component, the reason for this being its extremely high pozzuolanic activity as well as the fact that, under well defined conditions, it can work as an effective alkali activator (7).

The goal of the investigation was development of binding systems consisting of silica fume and sodium hydroxide. The main goal was establishment of a mixture resulting in a non-expansive composite.

Experimental

Silica fume from the production of silicium with a SiO_2 content of 95%, a density of 2200 $kg \cdot m^{-3}$ and a specific surface of 19600 $m^2 \cdot kg^{-1}$ was used. As an alkali component, sodium hydroxide according to the STN 68 4710 (8) was used. The quality of Na_2SiF_6 used corresponded to the requirements of the ON 65 3130 (9). The quality of the silica sand used corresponded to the STN 72 1208 (10). The ratio of its fine to medium fractions was 3:1.

Twenty-three mixtures of silica sand, silica fume, sodium hydroxide, and water were tested to determine the composition giving the best required properties. The proportion of sand was kept constant; the other components were variables.

The mixtures were mixed for 3 min, and cylindrical specimens of 30 mm in diameter and height were prepared. Vibration was used as the compaction procedure. The specimens were demolded after seven days of storage in the air and additionally cured at a temperature of 20 ± 2°C and a relative humidity of about 50%.

Besides the above-mentioned main components of the mixtures studied, an admixture of Na_2SiF_6 was used in some cases. The purpose of this was to study the possibility of accelerating the hardening process of the composite according to the reaction:

$$4\,NaOH + 2\,SiO_2 + 4\,H_2O + Na_2\,SiF_6 \rightarrow 6\,NaF + 3\,Si(OH)_4$$

which is a modification of the reaction:

$$2\,Na_2SiO_3 + 6\,H_2O + Na_2SiF_6 \rightarrow 6\,NaF + 3\,Si(OH)_4$$

The $Si(OH)_4$ gel produced should accelerate the hardening process of the system (11).

The composition of the composite was also evaluated on the basis of the matrix content, the packing coefficient α (12), which is often used for evaluating the quality of concrete. It was calculated by the formula:

$$\alpha = \frac{V_m}{V_v}$$

where V_m is the volume of the matrix, in m^3, and V_v is the voids volume of sand in a compacted state, in m^3.

The volume of matrix V_m can be calculated as:

$$V_m = \frac{W}{\rho_W} + \frac{SF}{\rho_{SF}} + \frac{N}{\rho_N}$$

where W, SF, and N is the dosage of water, silica fume and NaOH, respectively, in kg, and ρ_W, ρ_{SF}, and ρ_N is the density of water, silica fume, and NaOH, respectively, in kg·m^{-3}.

The volume of voids V_v can be calculated as:

$$V_V = \frac{S}{\rho_{UWC}} \cdot \frac{V_{CC}}{100}$$

where ρ_{UWC} is the unit weight of sand in a compacted state, in kg·m^{-3}, and V_{CC} is the voids content of sand in a compacted state, in percentages.

The voids content of sand in a compacted state, in percentages, can be calculated as:

$$V_{CC} = \frac{\rho_0 - \rho_{UWC}}{\rho_0} \cdot 100$$

where ρ_0 is the bulk density of the sand, in kg·m^{-3}.

The following properties of the test specimens were studied: appearance, changes in volume, compressive strength, bulk density, hydration products using XRD (Diffractograph Phillips) and DTA (Derivatograph G 425), and their morphology by SEM (Tesla BS 301).

Results and Discussion

It was found that the specimens expanded if the composition of the mixture was unsuitable. Expansion occurred if the content of NaOH was over 20% (related to the weight of the silica fume) and the water to cement ratio was over 0.75. The expansion of the composite had begun already during the hardening in the mold; an "overgrowth" matrix was formed, and its expansion continued after the demolding of the specimens. The specimens made from mixtures containing 20% of NaOH or less had a stable volume.

The results given in Table 1 show that the best compressive strengths were achieved by specimens not containing Na_2SiF_6. The compressive strength data of specimens "G" and "GX" show the positive effect of the lower water-to-solid ratio (water/silica fume + NaOH).

A comparison of the composite matrix volume (silica fume + NaOH + water) and voids volume of the compacted sand shows a large excess of matrix. While the composite "G" has an excess of $\alpha = 1.32$, the composite "GX" has only $\alpha = 1.20$. The lower values of the compressive strength of the composite "HX" compared to those of composite "GX" are possible due to the relatively low volume of the matrix ($\alpha = 1.05$). This also resulted in the decreased workability and compactibility of the mixture.

It seems that the optimal amount of matrix in the system studied is somewhat higher than in concrete. Optimal values of packing coefficient α for concrete are given between 1.05 and 1.10.

The application of DTA and XRD to the study on hydration products formed in the composites was unsuccessful. For example, the DTA curve showed only a large endothermic effect with a peak at 110°C, which probably corresponds to the thermal decomposition of the alkali-silica reaction products, and the endothermic effect with a peak at 560°C, which is typical for β-SiO_2 in the silica sand used. It is well known that the methods applied for the studying of amorphous materials are not suitable. Their lack of success demonstrates that

TABLE 1
Composition, bulk density, and compressive strength of alkali-silica composites and the packing coefficient.

Designation	Curing time (days)	$\frac{\text{Water}}{\text{SF + NaOH}}$	Dosage: NaOH (related to the weight of silica fume) (%)	Dosage: Na_2SiF_6 (related to the weight of silica fume + NaOH) (%)	Bulk density ($kg \cdot m^{-3}$)	Compressive strength (MPa)	Packing coefficient α
G	7	0.93	20	—	1789	9.9	1.32
	28				1743	38.4	
	112				1722	53.4	
GX	7	0.83		—	1933	11.1	1.20
	28				1860	61.6	
	112				1862	61.9	
HX	7	0.78		—	1857	13.5	1.05
	28				1800	50.0	
	112				1819	50.5	
GFA	7	0.93		4	1852	11.0	—
	27				1803	47.6	
	112				1807	49.5	
GFB	7			8	1889	16.2	—
	28				1809	29.1	
	112				1786	30.2	
GFC	7			15	1853	11.2	—
	28				1785	23.5	
	112				1784	24.1	
GXFA	7	0.83		4	1856	17.5	—
	28				1748	37.1	
	112				1789	37.4	
GXFB	7			8	1838	15.4	—
	28				1761	19.8	
	112				1710	20.1	
GXFC	7			15	1812	11.1	—
	28				1734	11.6	
	112				1710	19.1	
HXFA	7	0.78		4	1749	19.5	—
	28				1746	33.7	
	112				1709	35.6	
HXFB	7			8	1724	19.9	—
	28				1706	31.9	
	112				1679	33.1	
HXFC	7			15	1713	14.0	—
	28				1679	14.5	
	112				1660	19.9	

alkali-silicate reaction products formed in the composites studied were amorphous or nearly amorphous.

The amorphous state of the hydration products has been indirectly confirmed by SEM (Fig.

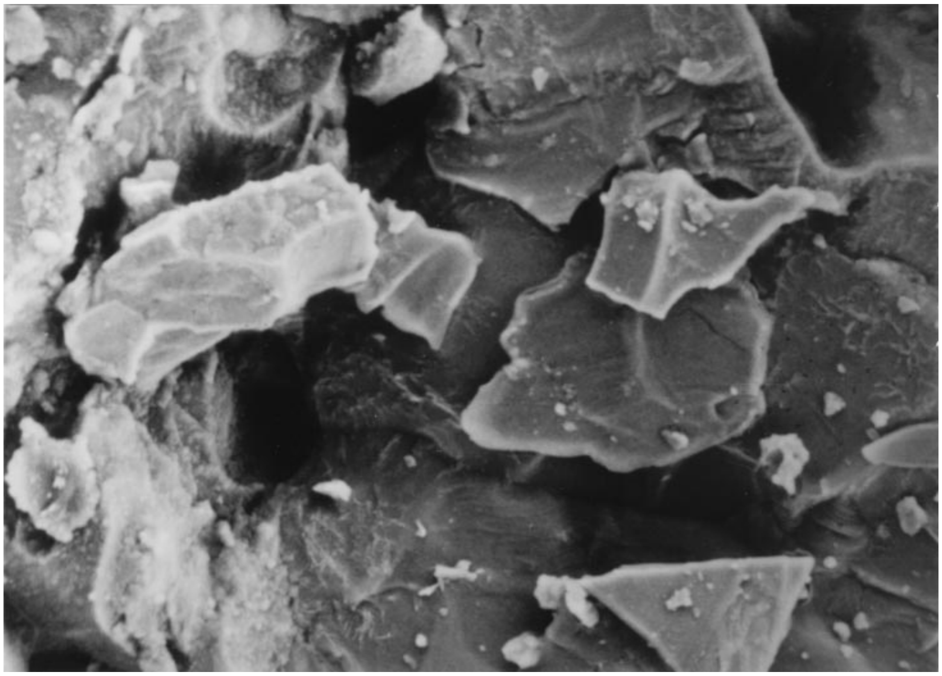

FIG. 1.
SEM of composite GX cured 28 days in the air. Magnification ×500

1). It represents a material without a distinct morphology occuring in the space between the grains of sand.

The reaction products are probably related to the alkali silicate hydrates, which usually occur in concrete affected by an alkali-silica reaction (13). The fact that silica fume and opal behave similarly when reacting with an alkaline solution is confirmed by the above-mentioned finding. This similarity even includes the formation of a product called expansive alkali-silica complex. Its development is considered due to the observed “overgrowth” of the matrix. According to the data obtained using an optimal composition of the mixtures, the effect of the complex could be controlled or its formation eliminated. Its management is an open issue which needs to be resolved through more detailed studies.

Evidently, the known water solubility of the observed alkali-silica products found in the composites studied was the reason for the fact that these materials were not durable in water (absence of hydraulicity). This property of the silica fume–sodium hydroxide systems seems to be a significant disadvantage.

Conclusion

It has been found that certain compositions of silica fume, sodium hydroxide, and water could represent an effective binding system. Using optimal ratios of the components, composites based on these binding systems can reach values of compressive strength comparable to those of Portland cement-based materials. This, however, is only valid for composites hardened in air. The water instability of the composites based on the studied binding system represents the system's significant failure. This instablility obstructs utilization of the binding potential. This disadvantage is evidently caused by the water solubility of the alkali silicates formed.

Preliminary results showed that improvement of the binding system studied can be achieved using basic blast furnace slag and silica fume alkali activator. This is the aim of further studies.

Acknowledgment

The authors are grateful to the Slovak Grant Agency for Science (Grant No. 12025/95) for partial support of this work.

References

1. S. Diamond, Cem. Concr. Res. 6, 549 (1976).
2. R. Helmuth and D. Stark, Materials Science of Concrete III, J. Skalny (ed.), p.31. The American Ceramics Society, Westerville, 1992.
3. V.V. Paturojev, Polymer Concretes (in Russian), Strojizdat, Moscow, 1987.
4. B.D. Toturbjev, Building Materials Based on Sodium Silicate Composites (in Russian), Strojizdat, Moscow.
5. J. Brandötetr, O. Meluzin, and J. Kohut, Stavivo 64, 182 (1986).
6. F. Škvára, Stavivo 65, 189 (1987).
7. V. Živica, Cem. Concr. Res. 23, 1215 (1993).
8. STN 68 4710 Sodium hydroxide (in Czech).
9. ON 65 3130 Sodium fluoro-silicate (in Czech).
10. STN 72 1208 Standard sands (in Czech).
11. A.V. Volženskij, J.S. Burov, and V.S. Kolokolnikov, Inorganic Binders (in Russian), Strojizdat, Moscow, 1979.
12. S. Bechynì, Concrete Engineering I, Concrete Technology, Vol. II (in Czech), SNTL, Prague, 1957.
13. H. Wang and J.E. Gillot, Mag. Concr. Res. 44, 235 (1992).