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Effect of silica fume, metakaolin, and low-calcium fly ash on chemical resistance of concrete

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Abstract

Effects of aggressive chemical environments were evaluated on the mortars prepared with ordinary portland cement (OPC) and silica fume (SF)/metakaolin (MK)/low-calcium fly ash at various replacement levels. The natural adverse chemical environmental conditions were simulated using sulfuric acid, hydrochloric acid, nitric acid, acetic acid, phosphoric acid, and a mixture of sodium and magnesium sulfates. Chemical resistance information was used in conjunction with compressive strength measurements to propose realistic OPC/mineral admixture proportions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Durability; Stability; Metakaolin; Pozzolan; Silica fume

1. Introduction

This study is a part of investigations of the utilization of supplementary cementitious materials (by-product materials) to prepare cementitious materials with adequate to superior long-term durability [1]. Concrete is one of the most widely used construction materials, because of its good durability to cost ratio. However, when subjected to severe environments its durability can significantly decline due to corrosion of embedded reinforcement and/or degradation of the concrete. Polymer modified mortars using synthetic rubber latexes and thermoplastic emulsions are known as chemically resistant concrete materials [2]. In recent years, polymer-based concrete materials have not been widely used due to environmental restrictions. Instead, mineral admixtures or supplementary cementitious materials are commonly used in concrete because they may improve durability. Among the various mineral additives used in concrete mortars, silica fume (SF) is highly favored for its superior concrete durability properties [3–5]. There is now considerable evidence that fly ash and metakaolin (MK) similarly improve durability performance [6]. When used as a concrete admixture, these additives combine with calcium hydroxide liberated during the hydration of cement in concrete, to form additional cementitious compound, mainly calcium silicate hydrate (CSH). The resultant binder matrix is more chemically resistant, by virtue of its denser microscopic pore structure. Even though the advantages of using mineral admixtures to control chloride permeability have been studied extensively [6], the beneficial effects of these materials in various adverse chemical environments are not reported to any extent. Harrison [7] concluded that there was a slower rate of acid attack on concrete with reduced lime content, while Hobbs and Matthews [8] pointed out the importance of reducing W/C for resisting acid attack. Taylor [9] has described numerous methods of characterizing the durability of cement pastes. The present paper addresses this problem in a preliminary way, as modern-day concrete is found in chemical plants and also subjected to various adverse chemical environmental conditions. A specific method standardized in ASTM [10] has been a major tool used in the current study to evaluate resistance to acidic chemical environments.

2. Objective

There are two major objectives of the study:

1. To simulate the adverse chemical environments in which modern-day concrete mortars are used and study the

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chemical resistance of ordinary portland cement (OPC) mortars containing supplementary cementitious materials SF, fly ash, and MK in contrast to pure OPC, to these simulated conditions.

2. To propose a realistic mixture proportioning of portland cement: SF/MK/fly ash, based on the above study.

3. Experimental

3.1. Selection of materials

Portland cement (Type I, MRL code I 40) was used in all cement–mineral admixture (supplementary cementitious materials) paste/mortar preparation. One example of each siliceous or aluminosilicate materials, high grade SF (MRL code G 15), MK (supplied by Engelhard, MRL code J-53), and low-calcium fly ash (MRL code B 97) containing about 17 wt.% quartz, 11 wt.% mullite, and 70 wt.% soluble silicates [11], was used as a supplementary cementitious material. In addition to these materials, Ottawa sand (ASTM C-109 grading, MRL code D 55) was used as a fine aggregate to prepare mortars.

3.2. Preparation of test specimens

Mortars were prepared from various proportions of OPC, SF and MK/low-calcium fly ash (0–30 wt.% replacement), and fine aggregate (sand) in accordance with ASTM C-349 mortar procedures. Control mortars were prepared from pure Type I portland cement. Mortars were prepared with 0.36 and 0.40 W/S (water/cementitious solid) ratios. Table 1 gives the various compositions and W/S used for the preparation of hardened pastes and mortars. Compressive strengths of the hardened pastes (no aggregate added) were measured after curing for 28 days at 38°C with 95% RH. For paste preparation, 0.30, 0.36, and 0.40 W/S ratios were used. No chemical admixture was used for the paste or mortar preparation.

Table 1
Compositions of mortar preparations from OPC and mineral admixtures

Sample code	OPC (g)	Mineral admixture (g)			Sand (g)	W/S
		SF	MK	Fly ash		
C	100	–	–	–	300	0.36
S1	92.5	7.5	–	–	300	0.36
S2	85.0	15.0	–	–	300	0.36
S3	77.5	22.5	–	–	300	0.36
S4	70.0	30.0	–	–	300	0.36
S5	70.0	30.0	–	–	300	0.40
S6	85.0	15.0	–	–	300	0.40
S7	77.5	22.5	–	–	300	0.40
M1	92.5	–	7.5	–	300	0.36
M2	85.0	–	15.0	–	300	0.36
M3	77.5	–	22.5	–	300	0.36
M4	70.0	–	30.0	–	300	0.40
M5	85.0	–	15.0	–	300	0.40
M6	77.5	–	22.5	–	300	0.40
F1	92.5	–	–	7.5	300	0.36
F2	85.0	–	–	15.0	300	0.36
F3	77.5	–	–	22.5	300	0.36
F4	30.0	–	–	30.0	300	0.40

SF: Silica fume; MK: Metakaolin.
Measurements to propose realistic OPC/mineral admixture proportions.

Table 2
Compressive strengths obtained for pastes with different proportions of OPC and mineral admixtures

Sample code	OPC (g)	Mineral admixture (g)			W/S	28-day compressive strength (MPa)
		SF	MK	Fly ash		
C	100	–	–	–	0.36	91.00
S1	92.5	7.5	–	–	0.36	75.89
S2	85.0	15.0	–	–	0.36	75.79
S3	77.5	22.5	–	–	0.36	74.80
S4	85.0	15.0	–	–	0.40	64.89
S5	77.5	22.5	–	–	0.40	71.31
M1	92.5	–	7.5	–	0.36	94.92
M2	85.0	–	15.0	–	0.36	87.91
M3	77.5	–	22.5	–	0.36	90.25
M4	85.0	–	15.0	–	0.40	83.38
M5	77.5	–	22.5	–	0.40	97.82
F1	92.5	–	–	7.5	0.36	86.80
F2	85.0	–	–	15.0	0.36	69.65
F3	77.5	–	–	22.5	0.36	55.59
F4	80.0	–	–	20.0	0.36	60.29
F5	85.0	–	–	15.0	0.30	77.17
F6	70.0	–	–	30.0	0.30	36.66
F7	80	–	–	20	0.30	66.12
F8[a]	80	–	–	20	0.30	72.15

SF: Silica fume; MK: Metakaolin.

[a] Ash attritor milled for 15 min.

3.3. Simulation of chemical environmental conditions

The relative chemical resistance was determined in accordance with ASTM C-267 (standard test method for

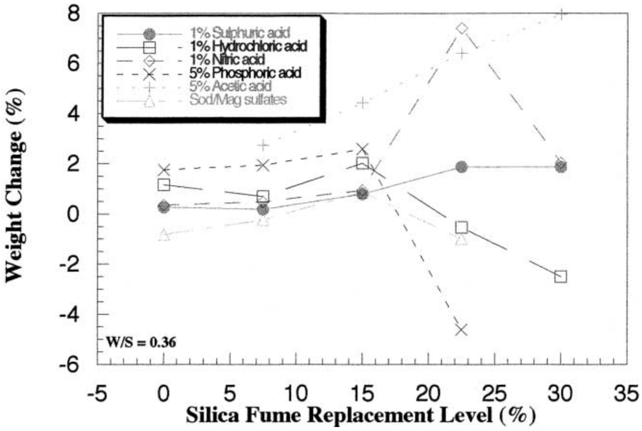

Fig. 1. Percentage weight change for mortars containing different SF replacement levels in various chemical environments.

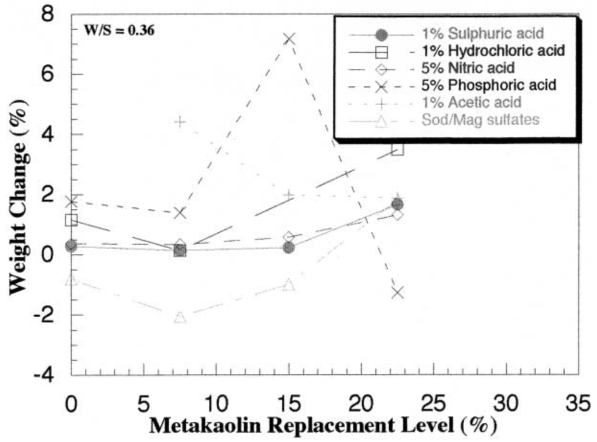

Fig. 2. Percentage weight change for mortars containing different MK replacement levels in various chemical environments.

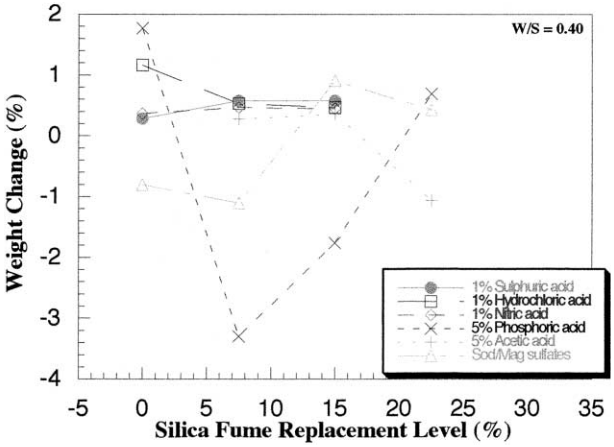

Fig. 4. Percentage weight change for mortars containing different SF replacement levels in various chemical environments.

chemical resistance of mortars) [10] and Taylor [9]. The aggressive chemical environmental conditions were simulated using the following chemicals: 1% sulfuric acid (H_2SO_4), 5% sulfuric acid (H_2SO_4), 1% hydrochloric acid (HCl), 1% nitric acid (HNO_3), 5% acetic acid (CH_3COOH), 5% phosphoric acid (H_3PO_4), and a mixture of sodium sulfate (Na_2SO_4), magnesium sulfate ($MgSO_4$) (0−175 mol each). The mortars were immersed in these aggressive chemical environments for 28 days. After 28-day immersion at room temperature, the attacked portions of the mortar specimens were cleaned with deionized water and then the chemical resistance was evaluated through measurement of the weight loss of the specimens determined as follows:

$$\text{weight loss (\%)} = \frac{W_1 - W_2}{W_1} \times 100$$

where W_1 is the weight (grams) of the specimens before immersion and W_2 is the weight (grams) of cleaned specimens after 28-day immersion.

4. Results and discussion

Deterioration of concrete may involve the removal of material from the surface by a dissolution mechanism or by expansion of material inside the concrete. In the first case, the aqueous environment dissolves soluble material and removes it from the concrete matrix. By this process, concrete becomes more porous, the rate of dissolution increases, and concrete may ultimately disintegrate. Dissolution may occur with and without chemical reaction. For example, hydrochloric acid present in the aqueous environment may react with calcium hydroxide from calcium chloride, which readily dissolves in the aqueous acid solution or removal of calcium hydroxide from the concrete

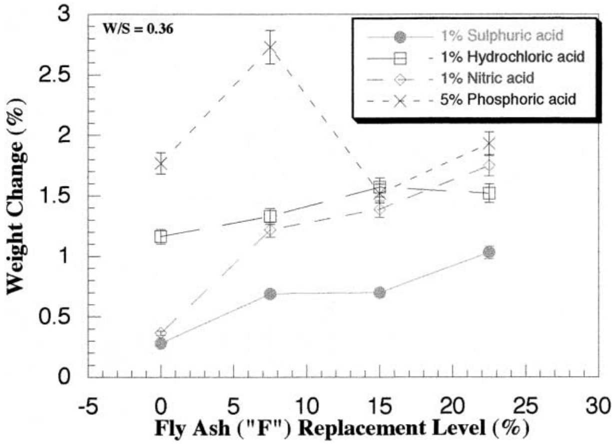

Fig. 3. Percentage weight change for mortars containing different low-calcium fly ash replacement levels in various chemical environments.

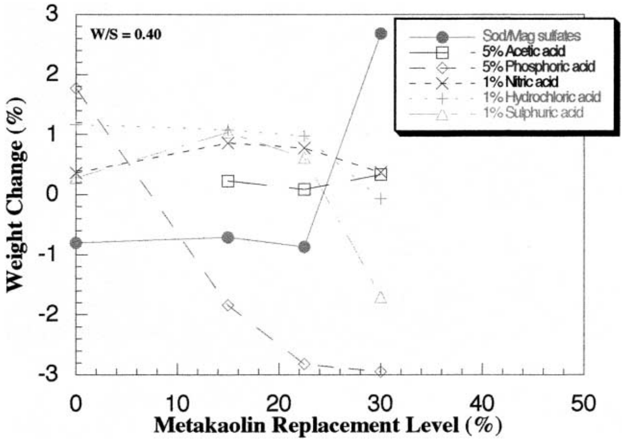

Fig. 5. Percentage weight change for mortars containing different MK replacement levels in various chemical environments.

Table 3
pH of chemical solutions before and after immersion of mortars

Solution number	Chemical solution	pH: Before immersion	pH: After 28-day immersion
1	1% H_2SO_4	1.46	11.72
2	5% H_2SO_4	1.03	6.95
3	1% HCl	1.46	11.82
4	1% HNO_3	1.40	11.76
5	1% H_3PO_4	1.55	4.59
6	5% CH_3COOH	2.50	11.57
7	Na/Mg sulfates (0.175 mol each)	8.90	11.89

may take place by permeating water. In the expansion mechanism, cracking and spalling result if materials formed by chemical reaction occupy a larger volume and are insoluble, causing a pressure increase within the concrete matrix. The classic example of deterioration by this mechanism is sulfate attack.

4.1. Effect of mineral admixtures on compressive strength

Compressive strength development of cement paste is strongly affected by the volume of CSH formed during cement hydration. The 28-day compressive strengths were measured for the pastes made from OPC/SF, OPC/MK, and OPC/low-calcium fly ash at various W/S ratios. The results of compressive strength measurement are given in Table 2. In the SF series, at the same W/S, 0–10 wt.% level produced high compressive strengths. In the MK series, all replacement levels developed good compressive strength. In the case of FA, 15–20 wt.% replacement levels produced better strength than 20–30 wt.% levels. The higher the replacement levels, the lower was the strength. W/S did not significantly influence the strength development in any of the series, except lower W/S improved the strength of fly ash mixtures.

In general, when comparing the same W/S, compressive strength decreased from MK to SF to FA. Even pastes made from fine FA did not produce compressive strength close to SF and MK series. Effective surface area and pozzolanicity of the mineral admixture influence hydration rate. The BET surface areas measured for SF, MK, and FA are 18.50, 12.45, and 1.13 m^2/g, respectively. FA (F8) was attritor milled for 15 min to increase the surface area. The surface area measured for this sample was 2.46 m^2/g. However, compressive strength for this fine variety is not comparable to SF and MK composition. The lower strength for FA may be attributed mainly to its low reactivity.

4.2. Effect on chemical resistance

The total weight change for mortars made from OPC/SF, OPC/MK, and OPC/low-calcium fly ash after 28-day immersion in various chemical environments is given in Figs. 1–5. Figs. 1–3 show the weight change for mortars made with 0.36 W/S and Figs. 4 and 5 show the weight change for the mortars made with 0.40 W/S. SF and MK series were remade with 0.40 W/S due to their high surface area, which resulted in poor particle packing in low W/S.

4.3. pH of the chemical solutions

Theoretically, any environment with pH lower than 12.5 may be predicted to be aggressive because a reduction of the alkalinity of the pore fluid would, eventually, lead to destabilization of the cementitious products of hydration. Thus, from the standpoint of portland cement concrete, most industrial and natural waters can be categorized as aggressive. However, the rate of chemical attack on concrete will be a function of the pH of the aggressive fluid and the permeability of concrete. When the permeability of the concrete is low and the pH of the aggressive water is above 6, the rate of chemical attack is considered slow. Table 3 gives the pH of the chemical solutions before immersing the mortar cylinders and after the immersion of mortar cylinders for 28 days.

The pH of acidic solutions changed to alkaline pH after 28-day immersion except for the higher concentration, 5% sulfuric acid, and 5% phosphoric acid solutions. The pH of these two solutions remained acidic after 28-day immersion. Cylinders immersed in 5% sulfuric acid were completely damaged after 28-day immersion and all the series mortars showed high weight change in 5% phosphoric acid solution.

5. Conclusion

The results are preliminary, but show some interesting trends with respect to acid resistance. Substitution of SF, MK, or FA under certain conditions has been shown to increase the chemical resistance of such mortars over those made with plain portland cement. Mortars were relatively little affected by 1% hydrochloric acid, 1% sulfuric acid, and 1% nitric acid environments, but those mortars made from all three series showed poor resistance to higher acid concentrations: 5% sulfuric acid, 5% acetic acid, and 5% phosphoric acid environments. Chemical resistance increased in the order of SF to MK to FA series and decreased as the replacement level is increased from 0–10 wt.% replacement level to 15–30 wt.% level. Contrary to expectation, chemical resistance increased with change from 0.36 to 0.40 W/S ratios. Compressive strength increased in the order of FA to SF to MK. No significant change in compressive strength was found as a function of replacement level for SF and MK series. However, the compressive strength decreased as the FA replacement level increased. This clearly shows that low-calcium fly ash is less reactive than SF and MK and needs an external activation. Nevertheless, fly ash is as effective in chemical resistance as SF and MK. A general overall conclusion would be that it is important to evaluate a particular concrete formulation before predicting its performance in a special acid environment. At least under certain circumstances the addition of FA, SF, or MK can improve the acid resistance of concrete.

References

[1] D.M. Roy, Alkali-activated cements: Opportunities and challenges, Cem. Conc. Res. 29 (1999) 249–254.

[2] Y. Ohama, T. Moriwaki, K. Notoya, Chemical resistance of polymer-modified mortars using thermoplastic emulsions, Proceedings 3rd International Conference on the Durability of Building Materials and Components, Technical Research Centre of Finland. Espoo, Finland, 1984, pp. 289–298.

[3] N.S. Berke, Resistance of microsilica concrete to steel corrosion, erosion, and chemical attack, fly ash, silica fume, slag, and natural pozzolanas in concrete, Proceedings 3rd International Conference, Trondheim, Norway, Am. Concr. Inst., SP 114-42, (1989) 861–886.

[4] T.A. Durning, M.C. Hicks, Using microsilica to increase concrete's resistance to aggressive chemicals, Concr. Int. 14 (3) (1991) 42–48.

[5] J.T. Wolsiefer Sr., Silica fume concrete: A solution to steel reinforcement corrosion in concrete, 2nd International Conference on Concrete Durability, Montreal Canada, Am. Concr. Inst., SP 126 (1991) 527–553.

[6] W.E. Ellis Jr., E.H. Riggs, W.B. Butler, Comparative results of utilization of fly ash, silica fume, and GGBFS in reducing the chloride permeability of concrete, 2nd International Conference on Concrete Durability, Montreal Canada, Am. Concr. Inst., SP 126 (1991) 443–458.

[7] W.H. Harrison, Durability of concrete in acidic soils and waters, Concrete 1 (2) (1987) 18–24.

[8] D.W. Hobbs, J.D. Matthews, Minimum requirements for concrete to resist chemical attack, in: D.W. Hobbs (Ed.), Minimum Requirements for Durable Concrete, British Cement Association, Telford Avenue, Crowthorne, Berks, UK, 1998, pp. 131–159.

[9] H.F.W. Taylor, Studies on the chemistry and microstructure of cement pastes, in: F.P. Glasser (Ed.), The Chemistry and Chemically Related Properties of Cement, Br. Ceram. Soc., Proc. 35 (1984) 65–82.

[10] ASTM C-267, American Society for Testing Materials, Volume 04.05, 1997.

[11] P. Arjunan, M.R. Silsbee, D.M. Roy, Quantitative determination of the crystalline and amorphous phases in low calcium fly ash, in: H. Justnes (Ed.), Proc. Xth Int. Congr. Chem. Cem., Gothenburg, Sweden, Amarkal and Congrex Gothenborg III, 1997 (3v 020, 4 pp.).