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PROPERTIES OF CEMENT-FLY ASH GROUT ADMIXED WITH BENTONITE, SILICA FUME, OR ORGANIC FIBER

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ABSTRACT

A detailed laboratory study was conducted to investigate the properties of cement-fly ash grout mixtures as barriers for isolation of hazardous and low-level radioactive wastes. In the grout studied, fly ash was used to replace 30 percent by mass of cement. Three additives including bentonite, silica fume, and polypropylene fiber were used individually in the grout mixes to improve the properties of the grouts in different aspects. The flowability, bleeding, and setting time of freshly mixed grouts were determined; and the unconfined compressive strength, pore size distribution, and water permeability were determined for hardened grouts at various curing durations up to 120 days. Finally, the durability of cement-fly ash grouts was carefully examined in terms of the changes in their physical properties after different levels of exposure to sulfate attack and wet-dry cycles. © *1997 Elsevier Science Ltd*

Introduction

Cement-based grouts have been used by geotechnical engineers for years to solve foundation problems such as infilling voids and improving watertightness of underground soil mass. In recent years, the use of cement grouts has been extended to environmental areas for sealing hazardous and low-level radioactive wastes. The literature indicate that grouting can perform its intended roles as a solidification agent and in stabilizing burial waste trenches, either as a remedial technique or at new installations [1,2].

In Taiwan, cement grouts have been proposed as sealing materials at waste disposal sites including hazardous waste landfills and low-level radioactive waste burial trenches. Previous studies have postulated the use of fly ash in the grout mixes [3]. The advantages of incorporating fly ash in the mix include reduction in cost, decrease in bleeding, increase in density, improved watertightness, and enhanced longevity of the grout. Current studies aim at formulating grout mixes to meet various requirements for adequate in-service performance. To achieve this, several additives including bentonite, silica fume, and polypropylene (PP) fiber were considered. Bentonite, a widely used material in traditional grouting applications, is included to reduce bleeding and improve imperviousness. Polypropylene fiber is introduced in the mix to minimize brittleness of the grout barrier thereby reducing the susceptibility to

TABLE 1

Physical and Chemical Properties of Fly Ash Used

$SiO_2 + Al_2O_3 + Fe_2O_3$, %	83.6
SO_3, %	0.35
Loss on ignition, %	7.42
Available alkalies, as Na_2O, %	0.69
Amount retained on No.325 sieve, %	19.3
Strength activity index with portland cement	
at 7 days, % of control	91.3
at 28 days, % of control	97.3
Water requirement, % of control	102.9
Specific gravity	2.21
pH	11.0

cracking in an underground environment. Silica fume, a by-product of the induction arc furnace in the silicon metal industry, is chosen because it decreases the porosity and permeability, and increases the strength, of the grout.

In a waste disposal site, the primary mechanism for the likely introduction of hazardous and/or radioactive elements into the environment is through physical and chemical deterioration of the waste barrier. It was the objective of this study to evaluate the physical properties of cement-fly ash grout. In addition, since grout barriers are subject to adverse environmental attack during their long term service, properties relating to the longevity were also investigated.

Materials and Procedure

Type I Portland Cement and fly ash were used in all the grout mixes in the study. The fly ash is a Class F fly ash obtained from Taichung power plant and the chemical and physical composition are shown in Table 1. The weight percentage of cement-fly ash in the mix was determined, in a preliminary study, to be 70-30 [3]. Three admixtures were added to the cement-fly ash mix individually to improve the grouts in different aspects. These were bentonite, silica fume, and polypropylene (PP) fiber. The bentonite used in the study was a sodium bentonite with a liquid limit of 600 to 700%. The moisture content as supplied was 9.0%, and the percent retained on #200 sieve, in a wet analysis, was 2.5. The PP fiber was a 3 Denier fiber having a length of approximately 10 mm, made by Hercules Co. The condensed silica fume has a Blaine fineness of 4,950 m^2/kg and 95% passing 45-μm sieve. The 70-30 cement-fly ash mix was used as control in the laboratory program. Grout mixtures were prepared with water/solid (water/cement + fly ash) ratios of 0.5, 0.7, 0.9 and 1.1 for each mixture. Table 2 summarizes the formulas used in the study with their notation used in this study. In these mixes, the amounts of silica fume and PP fiber are expressed as the weight percent of cement + fly ash, while the amount of bentonite is expressed as that of water.

Mixing of all grouts was accomplished using a 3-blade paddle mixer as suggested in ASTM C938. Bentonite was pre-hydrated in a 90% water/10% bentonite slurry and cured for 24 hours before it was introduced to the grout mix [4]. The amount of water used for preparing the slurry was deducted from that required for grout mixes. The exact amount of water was first poured into the mixer and the mixer started. Pre-mixed cement-fly ash (and

TABLE 2

Grout Formulas and Their Notation in This Study

Water/cement+fly ash	Additive and weight %	Notation
0.5	none	C5
	1% polypropylene fiber	F5
	1% (0.5%) bentonite	B5
	5% silica fume	S5
0.7	none	C7
	1% polypropylene fiber	F7
	1% (0.7%) bentonite	B7
	5% silica fume	S7
0.9	none	C9
	1% polypropylene fiber	F9
	1% (0.9%) bentonite	B9
	5% silica fume	S9
1.1	none	C11
	1% polypropylene fiber	F11
	1% (1.1%) bentonite	B11
	5% silica fume	S11

Note: The amount of bentonite is expressed as the weight percentage of water. Numbers in parenthesis convert that into weight percentage of solids.

silica fume, if used) was added into the mixer in two minutes and kept mixing for 3 minutes to complete mixing. Bentonite slurry or PP fiber was added one minute before the mixing was completed.

The laboratory program consisted of testing the engineering properties of flowability, final bleed, setting time, compressive strength, pore size distribution, and permeability of the grout mixes. The durability properties of the grout were also investigated. To accelerate deterioration, grout specimens were exposed to various cycles of wetting and drying and subjected to submersion in a 4.2-percent magnesium sulfate solution. They were then tested for changes in permeability, compressive strength and pore size distribution.

Results and Discussion

Flowability. The flowability is an important parameter relative to grout-mix design. Good flowability or low viscosity grouts are preferred for injection into fine fissures, or to increase the distance of penetration into fractures. Higher viscosity grouts might be preferred to limit penetration or fill wider fractures.

The flow of the grout was determined by a flow cone as recommended in ASTM C939. However, grouts with water/solid ratio of 0.5 were tested by flow table (ASTM C109) because the efflux time for these grouts exceeds 35 seconds. In the flow cone test, 1.725 liter of grout flows from the discharge tube of the cone and the time of efflux is recorded. Figure 1 summarizes the results. As expected, the flow of grouts increases with increase in water/solid ratio. If high flowability is desired for specific application, extra care should be

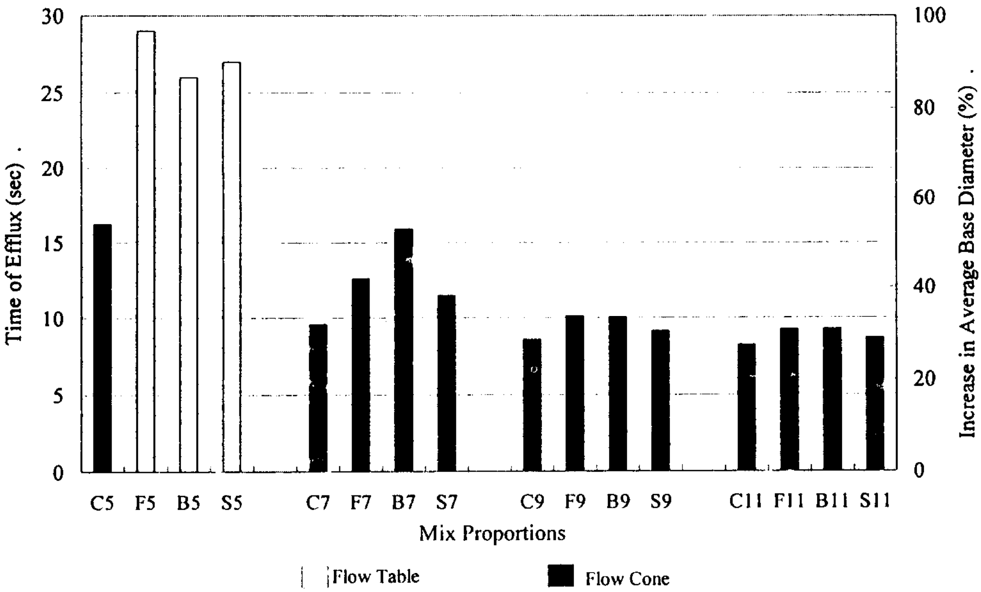

FIG. 1.
Flowability of freshly mixed grouts.

exercised in increasing the amount of water because this may increase the bleeding and adversely affect the engineering properties of the hardened grout.

It was also found that the addition of admixture tends to reduce the flow of grouts. The addition of PP fiber and bentonite shows greater effect on reduction in flow, especially at

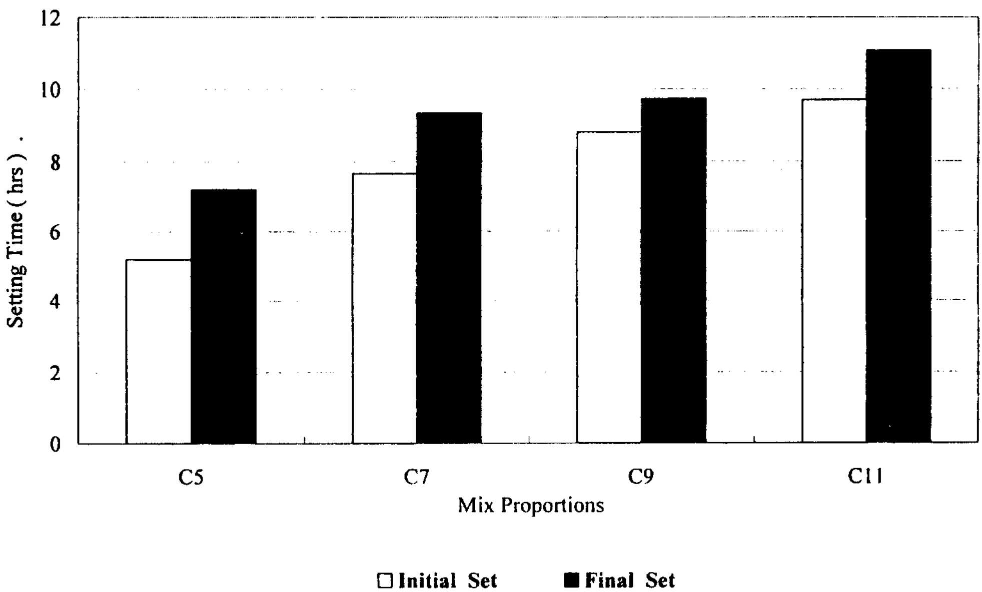

FIG. 2.
Setting time for control grouts.

low water/solid ratios. As the water/solid ratio increases, the influence of admixture on flow of the grout becomes negligible.

Setting Time. The initial setting time represents the time at which fresh grout can no longer be properly handled or injected; and final setting time approximates the time at which hardening and development of strength begin. In the field, the setting times provide a guide of available time for injection of a given batch before it must be discarded. Also, very short and controllable set time may be required for injection into a formation with a water flow to avoid washing the grout out before it hardens.

The initial and final setting times were determined using the vicat apparatus (ASTM C953). Results of the test on control grouts are shown in Figure 2. The initial setting time for water/solid ratio between 0.5 and 1.1 ranges from 5 to 9 hours respectively, and the final setting time ranges from 7 to 11 hours. These values are judged to be acceptable for general field applications. The 3 additives had negligible effect on the initial and final setting times.

Bleeding. Bleeding is the appearance of water on the surface before the grout has set. It is a form of segregation resulting from the inability of the solid particles to hold all mixing water in a dispersed state as the solids settle. Injection of grout mixes exhibiting excessive bleed may leave numerous uncontrolled open channels within the grouted mass, which leads to weakness, porosity, and a lack of durability [5].

Figure 3 shows in percent the final amount of bleeding of the grout mixes, as determined in accordance with ASTM C940. The water/solid ratio shows a great effect on the bleeding of the grout. The data indicate that silica fume and bentonite are both very effective in reducing bleeding. The addition of PP fiber however increases the final amount of bleeding. This can be attributed to the fact that PP fiber does not dissolve in the suspension; thus the amount of solid (cement + fly ash) particles is reduced in a unit volume of unset grout.

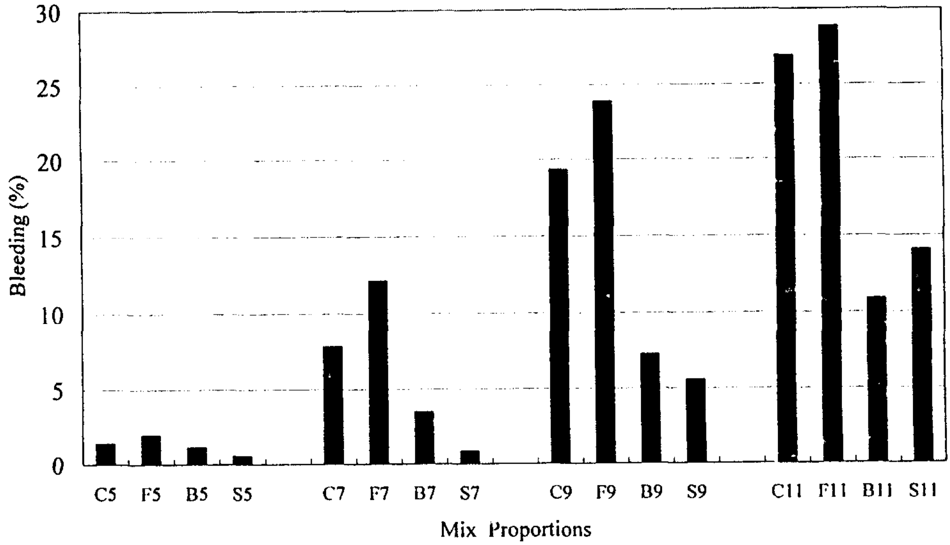

FIG. 3.
Final amount of bleeding for various grout mixes.

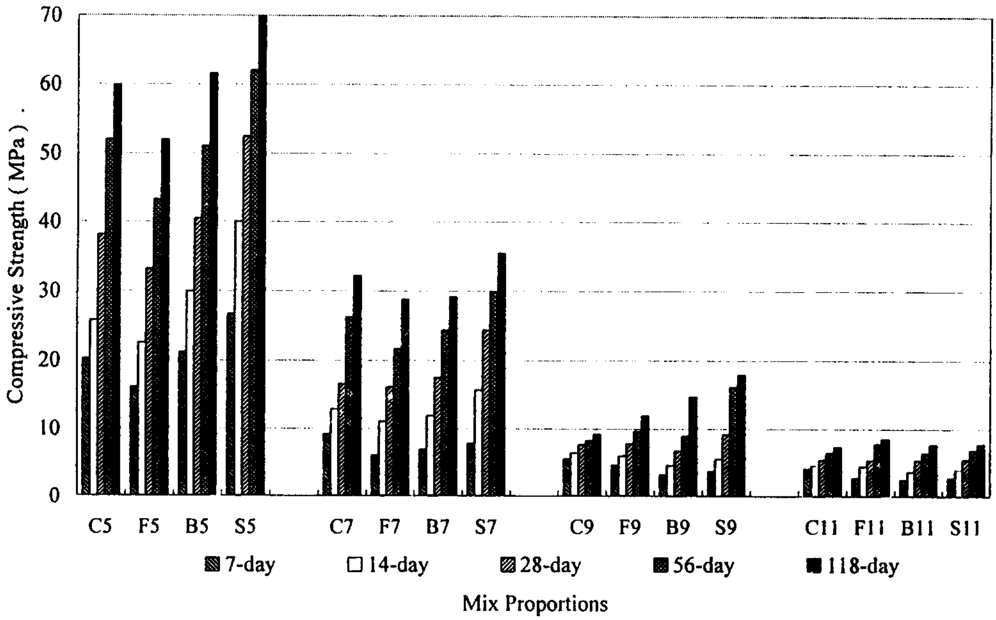

FIG. 4.
Compressive strength development for various grout mixes.

Compressive strength. The compressive strength of the grout is a property that relates directly to the structure of the cement paste, and provides a good indicator of its quality. Results of the unconfined compression strength tests on 50-mm grout cubes after moist curing up to 118 days are presented in Figure 4. It is observed that the addition of 5% silica fume increases the compressive strength of grouts. Also, as the water/solid ratio increases, the time required for silica fume to develop notable improvement in compressive strength increases. For example, with water/solid ratio of 0.5, the grout with silica fume is found to have greater compressive strength than the control grout as early as 7 days. However, at water/solid ratios of 0.7 and 0.9, it takes 14 and 28 days respectively to develop a notable increase in compressive strength between these grouts. For grouts with water/solid ratio of 1.1, this improvement in compressive strength becomes trivial.

The addition of PP fiber to the grout results in a reduction in compressive strength. This can be attributed to the weak planes formed at the interfaces between the fiber and grout matrix. At low water/solid ratios, grouts containing bentonite exhibit comparable values of compressive strength to that of the controls. As the water/solid ratio increases, bentonite shows a decreasing effect on the strength of the grout. This is because the addition of bentonite to the grout results in an increase in porosity (Fig. 5), especially at high water/solid ratios.

Pore Structure. The pores in cement grout form a continuum and the pore structure has been used in predicting permeability and durability of cement pastes [6,7]. In this study, pore size distributions of hardened grout were measured using a mercury intrusion porosimeter (MIP). The pores in the grout are divided into 3 categories based on their size. These are large capillary pores (greater than 0.05 μm diameter), medium capillary pores (0.01 to 0.05 μm diameter), and gel pores (smaller than 0.01 μm diameter). Capillary pores are considered

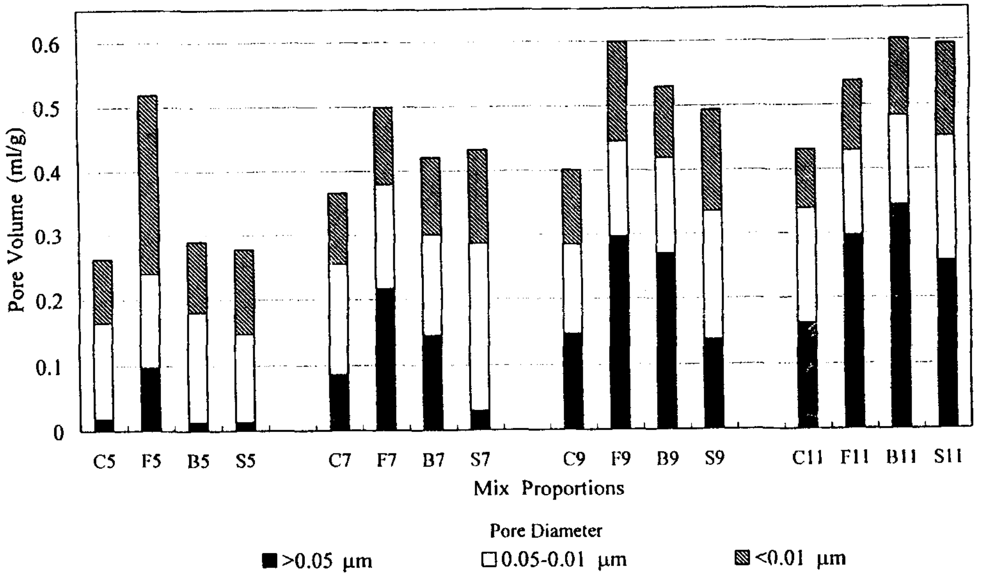

FIG. 5.
Pore volume of grouts at 28 days.

detrimental to the strength and impermeability of cement paste, while small gel pores are more important to drying shrinkage [8].

The volume of pores in each size category determined at 28 days is shown in Figure 5. It is found that PP fiber and bentonite have similar effects on the pore size distribution of grouts. The pore structure of grouts containing either PP fiber or bentonite is somewhat coarser than that of the control grout. This is illustrated in Figure 5 that the volume of large capillary pores increases with the addition of bentonite or PP fiber, while the volume of fine pores remains practically the same. Increases in the amount of large pores cause the grout to have high porosity which in turn may be detrimental to the engineering properties. Accordingly, it is recommended that the use of 1% bentonite be limited to grouts with water/solid ratios less than 0.7, although bentonite is very effective in reducing bleed of high water/solid ratio grouts.

As expected, the pore structure of grouts with silica fume is found to be finer than that of non-silica fume grouts. But this refinement in pore size is less substantial at high water/solid ratios.

Water Permeability. Water permeability tests were conducted on 28-day grout specimens using apparatus similar to the one described by Soongswang *et al.* [9]. Test specimens were 100 mm in diameter and 50 mm in height, and were coated with a 25-mm thick layer of epoxy by means of a casting mold. The prepared specimen was sealed between two acrylic platens with the aid of rubber gaskets. The permeability apparatus was then connected to the manometer tube and the coefficient of permeability was computed from the flow rate by using Darcy's Law. The measured coefficients of permeability for all grout mixes are presented in Figure 6. At water/solid ratios below 0.7, grouts containing PP fiber have their coefficient of permeability comparable to that of non-fiber grouts. Above water/solid ratio of 0.9, the coefficients of permeability of fiber-added grouts are two to three orders higher. Vondran [10] indicated that polymeric fibers have a log jamming effect on the pore structure

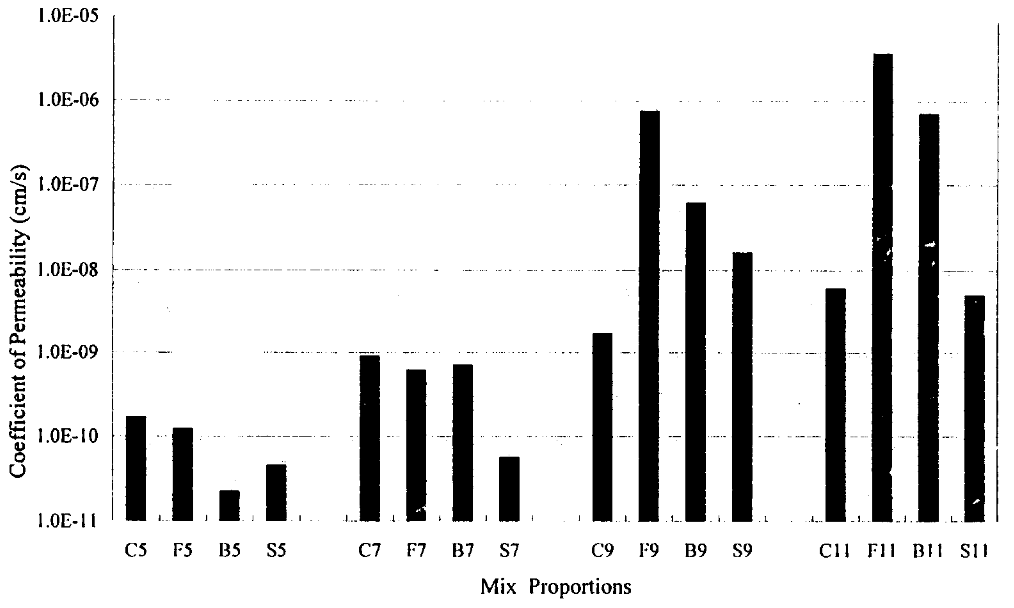

FIG. 6.
Coefficient of permeability of grouts at 28 days.

of concrete that reduces water permeability. It is expected that the PP fiber would improve the impermeability of grout mixes with lower fiber content. The effect of bentonite on the coefficient of permeability is similar to that of PP fiber, but the increase in permeability is less substantial than that obtained from PP fiber.

Due to the refinement of pores, the coefficients of permeability of grouts containing silica fume are approximately an order lower than those of control grouts. As the water/solid ratio increases, the decreasing effect on the coefficient of permeability becomes less substantial, as predictable from pore volume measurements.

The relationship between the coefficient of permeability and compressive strength of the grouts is plotted in Figure 7. This was intended to determine if it was possible to predict the coefficient of permeability from compressive strength for any given grout mixture. As shown in Figure 7, the strength-permeability relationship can be approximated by a hyperbolic curve. In the upper part of the curve, there is a sharp reduction in permeability associated with a small increase in strength. Therefore, if the demanding level of impermeability is specified for the grout, the corresponding requirement in strength may be obtained from the curve. For example, a typical criterion on the coefficient of permeability of 10^{-7} cm/sec for waste barrier applications would suggest a minimum strength of approximately 10 MPa or above. Similarly, the relationship established can provide an estimate of potential level of impermeability using strength test results.

Resistance to Sulfate Attack. After 28-day moist curing, grouts were submerged in 4.2% magnesium sulfate solution and then tested for compressive strength. The measured strengths after 28- and 90-day submersion were compared to those obtained from moist cured grouts. The difference in strength is expressed as a percentage of the compressive strength of the moist-cured grout in Figure 8. It can be observed that the control grouts with high water/solid ratio exhibit large increases in strength after exposure to sulfate attack. This

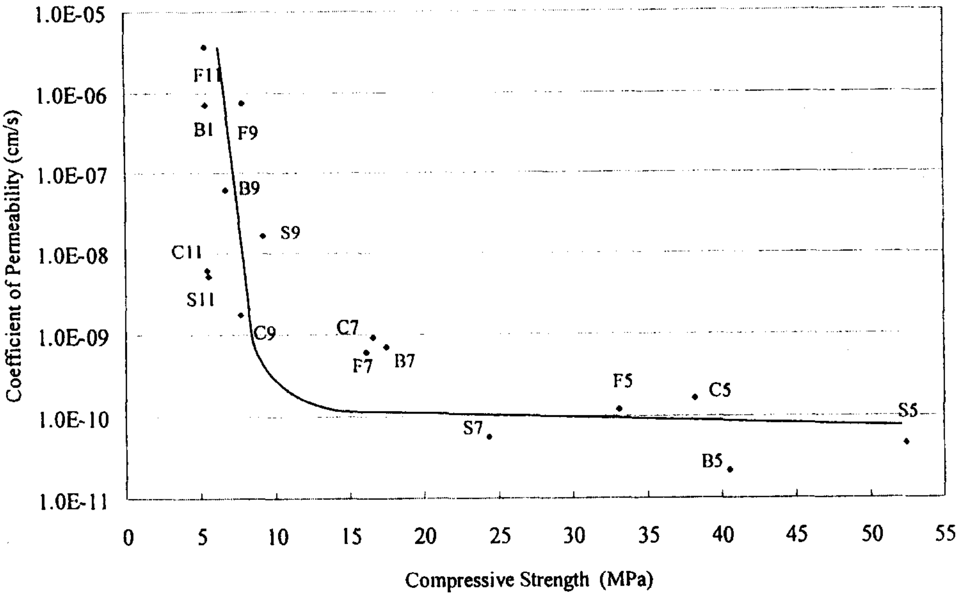

FIG. 7.
Coefficient of permeability versus compressive strength relationship for the studied grouts.

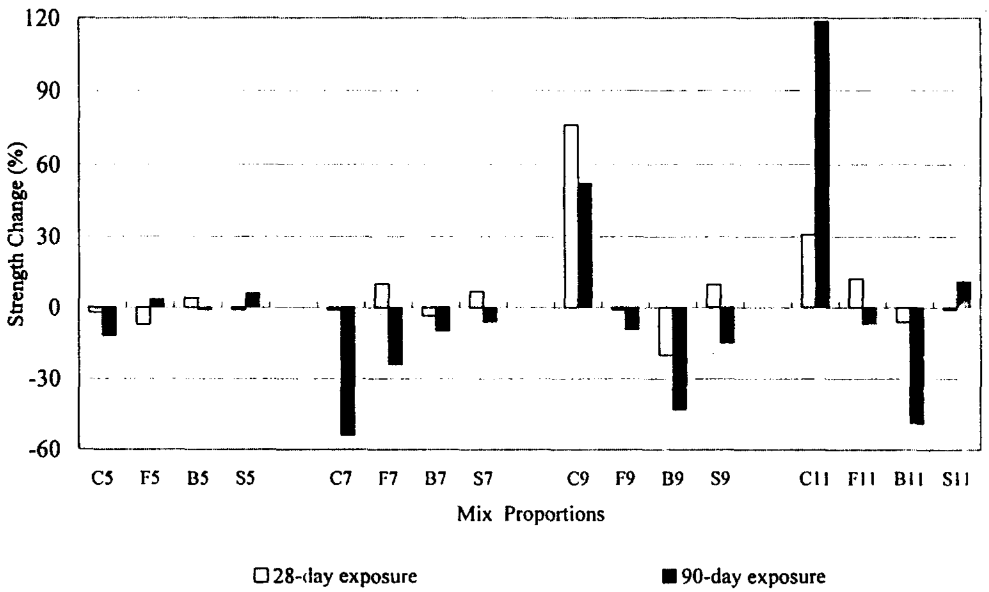

FIG. 8.
Strength change due to sulfate attack after two levels of exposure.

was unexpected and a hypothesis is proposed to account for this result. Since the chemical reaction between sulfate ions and hydration products of cement is expansive, the product of this expansive reaction may fill voids in the grout and create a temporary strengthening effect. The internal pressure resulting from the volume expansion may be restricted to the surface of the grout and become pronounced after a longer period of exposure depending on the water/solid ratio and mix composition. In fact, it was observed that there were fine cracks developed at the surface of grout specimens with high water/solid ratio after 28-day exposure. This hypothesis merits further experimental investigation.

Based on the discussion above, grout specimens showing either strength loss or temporary strength gain after exposure to sulfate environment are considered poor in resisting sulfate attack. Figure 8 shows that grouts with water/solid ratio of 0.5 have good resistance to sulfate attack. As the water/solid ratio increases, the control and bentonite-added grouts show obvious deterioration after exposure to sulfate solution. Grouts containing PP fiber and silica fume perform well under sulfate attack within the range of water/solid ratio investigated.

Resistance to Wetting-Drying Cycles. Following moist curing of 28 days, grouts were exposed to several cycles of wetting and drying. This was accomplished by alternately submerging grout specimens in water for 24 hours and drying in an oven maintained at 40 degrees C for 24 hours. Grouts were tested for their compressive strength after 5, 10, and 15 cycles of wetting and drying.

Results of compressive strength tests on grout specimens after exposure to different levels of wet-dry cycles are summarized in Figure 9. Generally, grouts with high water/solid ratios do not show any strength loss under wet-dry cycling. For grouts with water/solid ratios below 0.7, the addition of PP fiber and bentonite shows improving effects on compressive strength. The pozzolanic reaction between silica fume and calcium hydroxide leads to the

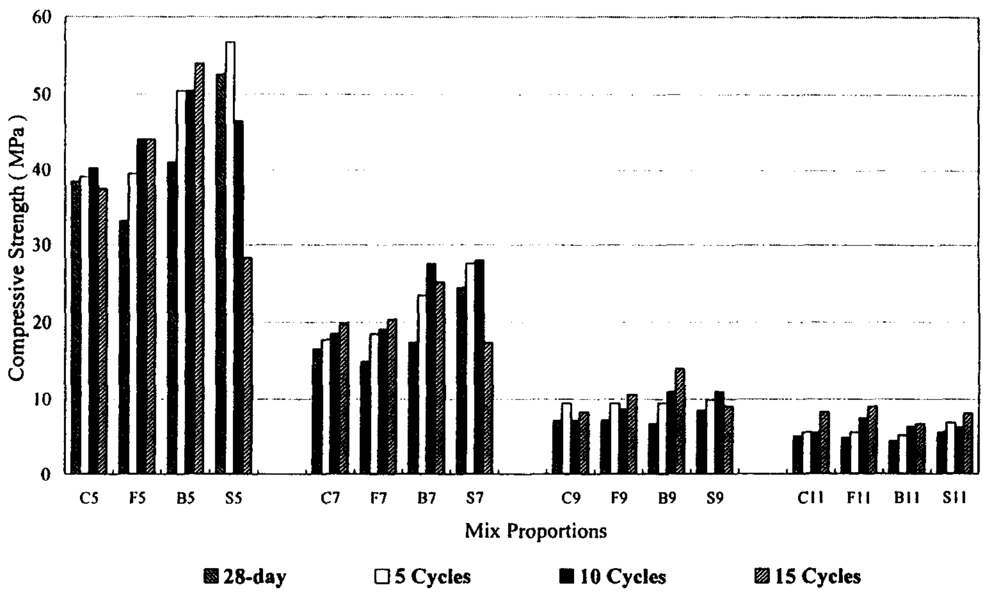

FIG. 9.
Compressive strength of grouts exposed to various wet-dry cycles.

formation of a very dense gel structure filled with brittle silicate compounds [11, 12]. As a result, grouts containing silica fume are more sensitive to shrinkage and subjected to expanding-shrinking damage as the water/solid ratio decreases. It is recommended that the amount of silica fume be reduced for grouts with water/solid ratios below 0.7 which are to be used in areas undergoing wet-dry cycles.

Summary and Conclusions

The results of laboratory studies aimed at formulating grout mixes for containment of low-level radioactive wastes have been presented. Three admixtures including polypropylene fiber, bentonite, and silica fume were evaluated for their effects on the engineering and durability properties of cement-fly ash grouts.

The use of 30% class F fly ash in the mixes produces economical grouts with reasonable compressive strength. The longevity of the grout and engineering properties can be improved by appropriately adding admixtures.

Addition of bentonite is effective in reducing the bleeding, but the accompanying high porosity in grouts may have damaging effects on engineering properties of the grout. As a result, it is recommended that 1% bentonite be admixed to grouts with water/solid ratios below 0.7.

Addition of polypropylene fiber significantly improves the grouts' resistance to changes in grout volume resulting from sulfate attack and wet-dry cycles. However, one percent polypropylene fiber also increases the permeability of the hardened grout, so the amount of fiber to be admixed in grouts needs be appropriately reduced.

Grouts containing silica fume show improved flowability, reduced bleeding, higher strength, and lower permeability in comparison to non-silica fume grouts. The addition of silica fume also improves the grout's resistance to sulfate attack, and the amount of silica fume can be adjusted to ensure adequate resistance to wet-dry cycles.

Acknowledgment

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