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PROPERTIES OF PORTLAND CEMENT CONCRETE CONTAINING FLY ASH AND CONDENSED SILICA-FUME

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ABSTRACT

Normal pozzolan additivies, due to their low surface area and reactivity are not able to improve early strengths and durability of concrete. The problem can be solved by using a mixture of normal and highly reactive pozzolans, such as condensed silica-fume. Results of an investigation are reported here in which 30 percent portland cement in concrete was replaced by an equal volume of fly ash, condensed silica-fume, or a 50:50 mixture of the two. Sand-to-gravel proportions were adjusted to obtain workable concretes having the same water cement ratio. As compared to the control concrete, the 7 and 28 days compressive strengths of the fly ash concretes were significantly lower, however, in the case of mixed-pozzolan addition, the 7-days strength was similar and the 28-days strength was higher. The differences in the pozzolanic activity of the additivies were confirmed by a parallel investigation involving determination of free lime and pore-size distribution of the cement pastes.

Vanlige pozzolaner vil pga deres lave spesifikke overflate og reaktivitet ikke forbedre verken betongens tidligfasthet eller dens bestandighet. Probelemt kan imidlertid løses ved a bruke en blanding av vanlige pozzolaner og høyreaktive pozzolaner så som silikastøv. Resultatene fra en undersøkelse er presentert hvor 30% av betongens portlandsement ble erstattet med et likt volum av henholdsivs flygeaske, silikastøv og en 50:50-blanding av disse to. Sammenliknet med kontroll-betongen vartrykkfastheten ved 7 og 28 døgn betydelig lavere for flygeaske-betongen, mens fastheten for tilsetning av blandede pozzolaner var den samme ved 7 døgn og høyere ved 28 døgn. Forskjellene i de tilsatte pozzolaners reaktivitet ble bekreftet i en parallell undersøkelse som omfattet bestemmelse av fri kalkinnhold og porestørrelsesfordeling i sementpasta.

Introduction

In most countries, the idea of adding slags and pozzolans such as fly ash to portland cement or portland cement concrete is widely practiced because it helps to reduce cost and conserve energy, resources, and the environment. It is well known that pozzolans are siliceous materials which, in the presence of moisture, and at normal temperature, react with lime to form cementitious calcium silicate hydrates. Since lime is a byproduct of the hydration of portland cement and since by itself lime is not cementitious, the addition of a pozzolan to portland cement concrete can result in improving the ultimate strength and durability of the product by transforming lime into calcium silicate hydrates.

At normal temperature, the lime-pozzolan reaction is very slow, the rate of reaction being dependent on the reactivity of the silica present which, in turn, depends on the surface area and degree of amorphousness of the material. Relatively inexpensive pozzolans such as volcanic ash and fly ash contain, besides glass, significant amount of crystalline matter. Also, whether interground with portland cement or added directly to concrete, the surface area of these pozzolans seldom exceeds 1 m^2/g. Although availability of lime from the hydration of portland cement begins soon after addition of water to the cement, it is due to the low surface area of the pozzolans that the pozzolanic reaction does not progress to a significant extent until after several weeks of hydration of the cement.

Most specifications for portland-pozzolan cements or for concrete containing pozzolans permit the use of up to 40 percent pozzolan by weight of total cementitious materials. However, for most structural applications except mass concrete, the pozzolan content is limited to 20-25 percent. This is because the early strengths, for instance at ages 3 and 7 days, are generally reduced in direct proportion to the amount of pozzolan present in the cement. Another drawback of portland-pozzolan concretes is the prolonged moist-curing needed for the pozzolanic reaction without which the potential benefits of high ultimate strength and superior chemical durability can not be realized.

Although normal pozzolans which are available in large quantities are not highly reactive, there are some highly reactive pozzolans which have recently come to the attention of researchers in the field of cement and concrete. Burning rice hulls and straw at low temperature yields a silica ash consisting of 85-90% amorphous silica with 50-60 m^2/g surface area. The pozzolanic characteristics of this rice-hull ash are described elsewhere (1). However, at present the amorphous rice hulls ash is not available in large quantities. Condensed silica-fume, a byproduct of the silicon and ferrosilicon industries, consists of 85-96% amorphous silica with 20-25 m^2/g surface area. The material is commercially available in considerable quantities, and its production and properties are discussed in detail below.

Condensed silica-fume is the byproduct of electric arc furnaces used for the production of silicon metal or alloys. Ferrosilicon alloys containing 50-75% Si are the most important alloys of silicon. The raw materials used for the production of ferrosilicon are usually 3-6 inch pieces of crushed quartz, coke, and iron ore. Reduction of quartzitic silica in the presence of carbon at temperatures on the order of 2000°C, in the areas between electrodes submerged in the charge, results in the formation of silicon. About 10-15% quartz in the charge is lost in the form of Si and SiO vapors which react with air to form SiO_2. Upon cooling the gases from the arc furnace, the SiO_2 fumes condense into very tiny spherical particles, composed essentially of amorphous silica.

The chemical composition of the condensed silica-fume from the ferrosilicon industry corresponds, generally, to 85-92% SiO_2, 0.5-3% Fe_2O_3, 1-3% alkalies, 1-2% carbon, and minor amounts of Al_2O_3, CaO, and MgO. The material from the silicon industry has lower iron content. Small variations in the chemical composition are not significant from standpoint of pozzolanic properties of a condensed silica-fume. However, what is significant is the fact that the product from both the silicon and the ferrosilicon industries contains more than 85% amorphous SiO_2, possessing high surface area. Nitrogen adsorption measurements show 20-25 m^2/g surface area of the material. The particle size analyses show individual spheres ranging from 0.01 to 0.3 μm, with about 70% < 0.1 μm. It is estimated that every year up to 500,000 tons and 200,000 tons of condensed silica-fume are available for disposal in the United States and Norway, respectively. Exceedingly fine particle size, and high bulk volume cause packaging and environmental difficulties in handling and disposal of the material.

The first investigations on the use of condensed silica-fume in Norway were carried out in the 1950's, and some of the field tests are now approx. 30 years. It was not until strict Norwegian regulations on environmental control were introduced some years ago, however, that more comprehensive research programs were started. Some of the results from these programs have recently been published (2).

Bache (3) reported compressive strengths of the order of 120 MPa at 14 days from a concrete mixture containing 133 Kg/m^3 of Norwegian condensed silica-fume, 400 Kg/m^3 portland cement, 100 Kg/m^3 water (0.19 ratio of water-to-cementitious materials), 13.5 Kg/m^3 superplasticizer, and specially-sized quartz sand and crushed granite. Due to the high cost of such concrete mixtures, this type of use for condensed silica-fume will be limited. The authors forsee a wider application of the material if it is used as a strength accelerator in portland cement concretes containing normal pozzolans. In this paper, the results of an investigation are given in which a mixture of fly ash and condensed silica-fume was used as an addition to a portland cement concrete. Properties of concretes containing no pozzolanic addition, fly ash only, or condensed silica-fume only are included for comparison purposes.

Material and Procedure

The chemical composition and surface area of the portland cement, fly ash and condensed silica-fume used in this investigation are shown in Table 1. The specific gravity of the portland cement, condensed silica-fume, and fly ash were 3.2, 2.2, and 2.4, respectively. The control concrete was designed for about 15 cm slump, and 25 MPa compressive strength at 28 days. The mix proportions of the control concrete corresponded to 300 Kg/m^3 cement content, 0.75 water-to-cement ratio, and 65:35 sand-to-coarse aggregate ratio by weight. In the concrete containing the condensed silica fume, 30 percent of the portland cement was replaced by an equal volume of the condensed silica-fume, and sand-to-coarse aggregate ratio was reversed. In the concrete containing the fly ash, 30 percent of the portland cement was replaced by an equal volume of fly ash, and the sand-to-coarse aggregate ratio was 50:50. In the concrete containing both the condesned silica fume and fly ash, equal volumes of these pozzolans were used to replace 30 percent portland cement. All concretes were made with a constant water to cementitious materials (cement + silica fume + fly ash) ratio of 0.75 by weight. The mix-proportions data and actual slumps obtained are shown in Table 2. In spite of the low slumps, the concretes containing the condensed silica-fume showed excellent workability.

For testing the compressive strength of concrete, 100 mm cube specimens

TABLE 1

Characteristics of Portland Cement and Pozzolanic Materials

	Portland Cement, %	Fly Ash, %	Condensed Silica-Fume, %
Chemical Composition:			
SiO_2	20.6	64.9	96.0
Al_2O_3	4.8	26.2	0.1
Fe_2O_3	2.9	3.3	0.6
CaO	63.6	2.2	0.1
MgO	2.5	-	0.2
SO_3	3.2	-	-
K_2O	1.1	-	0.4
Na_2O	0.4	1.1	0.1
Ignition Loss	0.7	4.5	1.7
Surface Area:			
Blaine, cm^2/g	3160	4000	-
BET, m^2/g	-	-	20

TABLE 2

Mix Proportions and Slump of Concrete

	Control Concrete	Concrete Containing Condensed Silica-Fume	Concrete Containing Fly Ash	Concrete Containing Both Pozzolans
Cement Content, Kg/m^3	300	210	210	210
Condensed Silica Fume, Kg/m^3	0	60	0	30
Fly Ash, Kg/m^3	0	0	60	30
Fine Aggregate, Kg/m^3	1268	683	975	683
Coarse Aggregate, Kg/m^3	683	1268	975	1268
Water, kg/m^3	222	202	208	205
Slump, cm	17	2½	13	5

were cast in accordance with Norwegian Code NS 427A. After 24 hours of normal curing in molds, the specimens were demolded and stored in water at 20^{o}C until the test age. Compressive strengths were measured from triplicate specimens at age 3, 7, 28, and 90 days. The data are shown in Table 3.

TABLE 3

Compressive Strength of Concrete

	3 Days		7 Days		28 Days		90 Days	
	MPa	Difference from the Control, %	MPa	Difference from the Control, %	MPa	Difference from the Control, %	MPa	Difference from the Control, %
Control Concrete	14.7	-	20.0	-	26.6	-	28.6	-
Concrete Containing Fly Ash	12.1	-18	17.8	-11	23.2	-12	27.6	-3
Concrete Containing Condensed Silica-fume	15.2	+3	24.4	+22	47.0	+77	56.2	+97
Concrete Containing Both Pozzolans	14.2	-3	20.2	+1	37.9	+42	43.3	+51

In order to study the characteristics of the hydrated cement pastes in the above concretes, neat cement pastes containing the same proportion of pozzolans and water were made in vacuum, cast into plastic vials, and tumbled for 24 hours to prevent bleeding. Thereafter, the hardened pastes were demolded and stored under moist conditions at room temperature until ready for testing. At age 7, 28, and 90 days, the paste specimens were crushed into small pieces, washed thoroughly with acetone to stop hydration, and dried at 70^{o}C under vacuum. The dried specimens were subjected to relative free lime content determination by ASTM Method C114, and pore size distribution analysis by mercury penetration technique. The free lime data are shown in Table 4, and the pore size analyses data are plotted in Figures 1-3.

Discussion of Results

From the data on compressive strengths of concrete in Table 3, it is obvious that the early strengths, viz. at 3, 7 and 28 days, of concretes containing the fly ash were significantly lower than the control portland cement concrete. At 90 days, however, the strength of the concrete containing the fly ash was similar to the control concrete. This is consistent with the well known fact that in the case of fly ash and natural pozzolans, in general, the pozzolanic reaction at normal temperature is too slow to yield improvements

TABLE 4

Free Lime Content of Cement Pastes, %

	7 Days	28 Days	90 Days
Control Portland Cement	15.0	16.9	18.9
Portland Cement Containing Fly Ash	11.8	13.2	13.4
Portland Cement Containing Condensed Silica-Fume	10.7	7.9	4.2
Portland Cement Containing Both Pozzolans	11.0	10.2	9.5

in the properties of the blended cement products at early ages. Therefore, prolonged moist curing of portland cement concretes is essential before the benefits expected from such pozzolanic additions become manifest.

As compared to the concrete containing the fly ash, the specimens containing the condensed silica-fume showed considerable higher strengths even at early ages of curing. For instance, the compressive strengths of the concretes containing the condensed silica-fume were higher by 22 and 77 percent at 7 and 28 days, respectively, than the control portland cement concrete, and the 90-days compressive strength was almost twice as much as the control. The data on compressive strengths of concrete containing both the fly ash and the condensed silica-fume showed that the strength at 3 days was similar to the control concrete, and was much higher at 28 and 90 days. Since in field practice, it is not difficult to cure concrete for 3 days before exposing it to environmental conditions, for many applications the value of the concept of using blends of highly reactive pozzolans with normal pozzolans, instead of normal pozzolans alone, is quite obvious.

In regard to differences in pozzolanic activity of the various pozzolans used in this investigation, the free lime analyses data of the hydrated cement pastes in Table 4 were, in general, found consistent with the concrete strength data. From the free lime in the control portland cement pastes, the free lime contents of the 7, 28, and 90-days old portland-fly ash pastes (containing 24 wt. percent fly ash) are calculated as 11.3, 12,8, and 14.3 percent, respectively. The actual free lime contents by the ASTM C114 were found to be 11.8, 13.2, and 13.4 percent, respectively. At 7 and 28 days, the actual free lime contents were somewhat higher than the theoretical values. This was probably due to some acceleration of hydration of the calcium silicate compounds of portland cement in the presence of reactive silica. The free lime contents, however, clearly show that little or no pozzolanic activity occurred in the portland-fly ash pastes until 28 days. On the contrary, considerably lower values of free lime in the pastes containing the silica-fume or both fly ash and silica-fume, were indicative of high pozzolanic activity even at 7 and 28 days. Neglecting the acceleration in the rate of hydration of portland cement compounds in the presence reactive silica, the calculated free lime contents at 7, 28, and 90 days for the portland silica-fume pastes (containing 22 wt. percent silica-fume) are 11.7, 13.2, and 14.8 percent, respectively. The actual free lime contents were found as 10.7, 7.9, and 4.2 percent, respectively, thus reflecting very high pozzolanic activity at all ages including

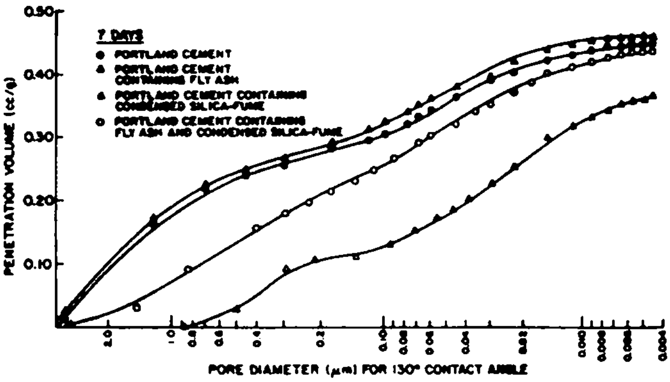

FIGURE 1

Pore Size Distribution of 7 Days Old Hydrated Paste

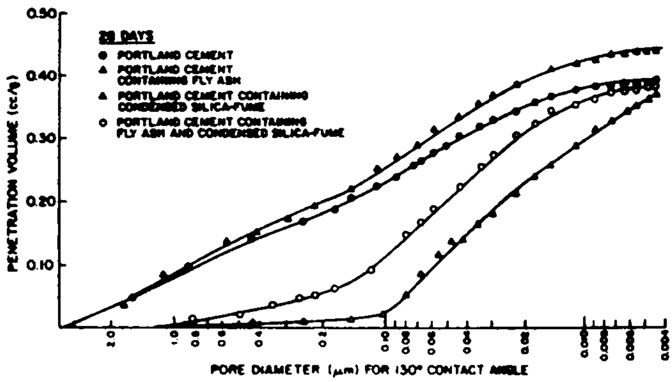

FIGURE 2

Pore Size Distribution of 28 Days Old Hydrated Paste

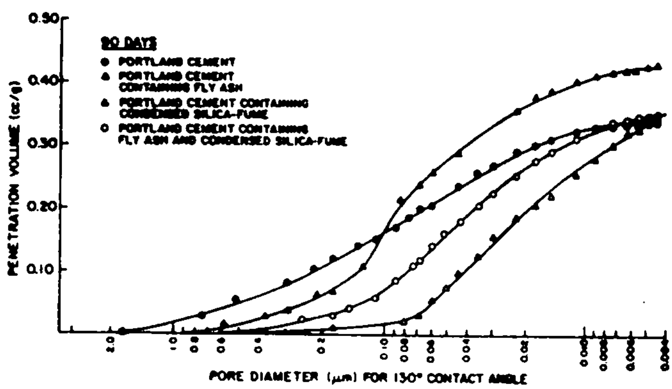

FIGURE 3

Pore Size Distribution of 90 Days Old Hydrated Paste

7 days. The free lime contents of the pastes containing both the condensed silica-fume and fly ash were found consistent with the values expected from such mixtures of the two types of pozzolans.

The pore size distribution data of the various pastes at 7, 28, and 90 days, plotted in Figures 1, 2, and 3, respectively, help to explain the differences in strength characteristics of various concrete mixtures. Investigation by Mehta (4), and Regourd et al (5) showed that the calcium silicate hydrates formed as a result of pozzolanic reaction were less dense than the similar products formed by portland cement hydration and, therefore, caused pore-size reduction. In an investigation involving a volcanic ash, Mehta (6) reported that the volume of large pores (> 0.1 μm) in hydrated cement pastes adversely affected the compressive strength of mortars made with the same water-to-cement ratio. It was concluded that the conversion of large pores to finer pores (< 0.1 μm) as a result of the pozzolanic reaction played an important part in enhancing the strength of portland-pozzolan cements (6).

From Figures 1 and 2, it is evident that at 7 and 28 days both, the total volume of mercury-penetratable pores and the volume of large pores (> 0.1 μm) were somewhat higher for the portland-fly ash pastes than for the control portlant cement pastes. Correspondingly, at these ages, the concretes made from the portland-fly ash cement, at the same water-cement ratio, showed lower strengths than the control portland cement concrete. At 90 days, although the total penetrable pore volume of the portland-fly ash cement paste was much higher than the control portland cement, the volume of large pores (> 0.1 μm) was similar and, consequently, the concrete strengths were similar. In the case of portland-silica-fume paste, at 7 days the volume of large pores was only 0.123 cc/g against 0.30 cc/g for the portland cement paste, and the corresponding concrete strength was 22 percent greater for the former. At 28 and 90 days, although the total penetrable pore volumes were similar for the two pastes, there were hardly any large pores in the portland-silica-fume paste as compared with 0.225 and 0.17 cc/g (> 0.1 μm), respectively, for the control portland cement. These differences in the volume of large pores in the cement pastes, although difficult to relate directly with concrete properties, are nevertheless reflected in the strengths of corresponding concretes. The presence of the condensed silica-fume in the portland-fly ash mixtures caused considerable reduction in the volume of large pores at all ages, and was thus instrumental in causing the beneficial effect observed on concrete strengths.

Conclusion

The replacement of portland cement by 30 vol. percent of a fly ash caused significant reductions in the compressive strength of 7 and 28 days old concretes. Only at 90 days, the strength of the fly ash concrete was similar to the control concrete. When a condensed silica-fume was used instead of fly ash, the sand-to-gravel proportions were altered in order to produce workable concretes having the same water-cement ratio. As compared to the control, the concretes containing the condensed silica-fume showed 22, 77, and 97 percent higher strengths at 7, 28, and 90 days respectively. When equal volumes of fly ash and condensed silica-fume were used to replace 30 vol. percent portland cement, the 3-days concrete strength was similar while the 28-days and 90-days strengths were respectively, 42 and 51 percent higher than the control. It can be concluded, therefore, that from the standpoint of early concrete strengths, it is better to use mixtures of low and high surface-area pozzolans, such as fly ash and condensed silica-fume, than using a normal pozzolan alone. Differences in strengths of concretes could be explained on the basis of free lime content and pore-size distribution of the corresponding cement pastes. Reduction in the volume of large pores (> 0.1 μm) was observed with the progress of the pozzolanic reaction. High concrete strengths were generally associated with lower volume of large pores in the cement paste.

References

1. P. K. Mehta, "Properties of Blended Cements Made from Rice Husk Ash". ACI Journal, Vol. 74, No. 9, pp. 440-442, 1977.

2. K. E. Loland and O. E. Gjorv, "Silica Concrete", Nordisk Betong, Vol. 25, No. 6, pp. 5-10, 1981.

3. H. H. Bache, "Densified Cement Ultra-Fine-Particle-Based Materials", Paper presented at the ACI Symp. on Developments in the Use of Super-Plasticizers, Ottawa, 1981.

4. P. K. Mehta, "Sulfate Resistance of Blended Portland Cements Containing Pozzolans and Granulated Blastfurnace Slag", Proc. 5th International Symp. on Concrete Technology, University of Nuevo Leon, Mexico, pp. 35-50, 1981.

5. M. Regourd, B. Mortureux, and E. Gautier, "Hydraulic Reactivity of Various Pozzolans", ibid, pp. 1-14, 1981.

6. P. K. Mehta, "Studies on Blended Portland Cements Containing Santorin Earth", Cement and Concrete Res., Vol. 11, pp. 507-518, 1981.

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