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Fly Ash, Silica Fume, Slag & Other Mineral By-Products in Concrete I

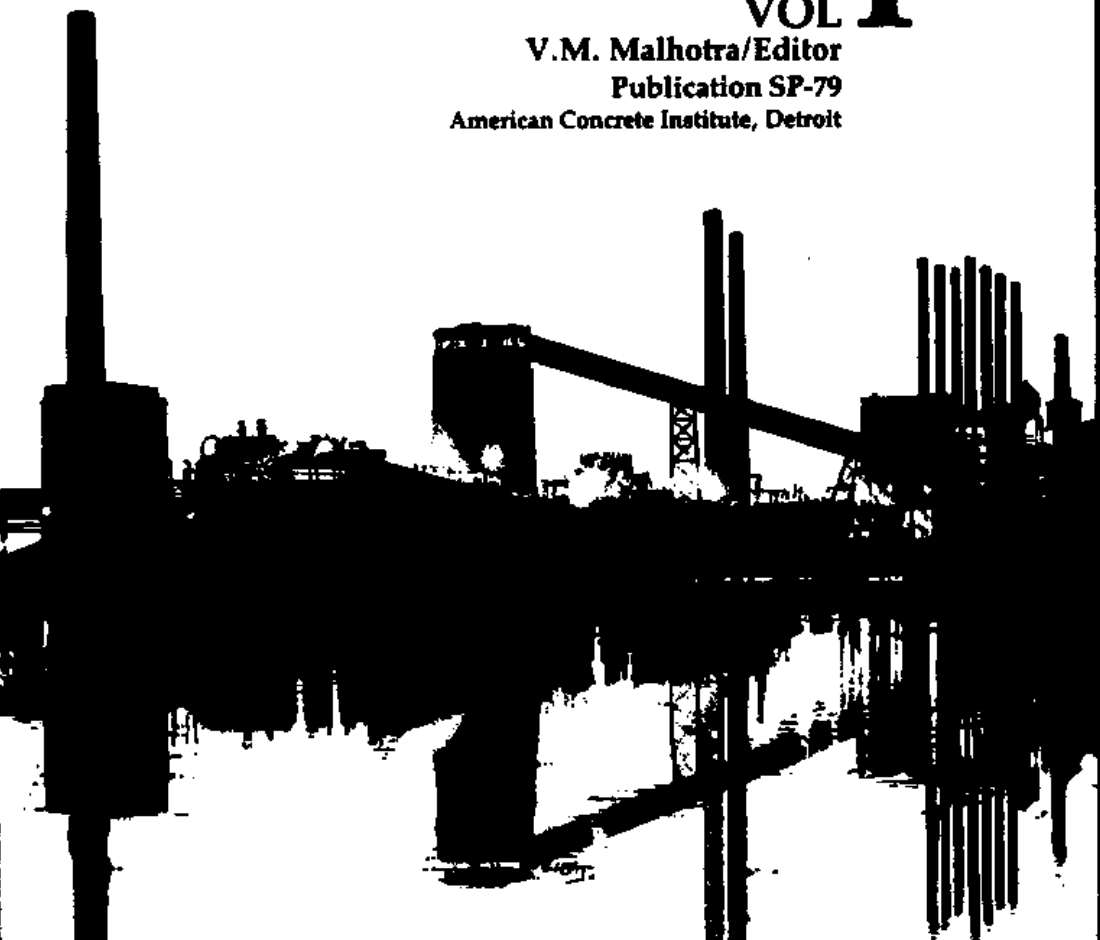


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Pozzolanic Property of Natural and Synthetic Pozzolans: A Comparative Study

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Synopsis: Three natural pozzolans, a fly ash, and a sample of silica fume have been characterized by means of chemical analysis and nitrogen adsorption. The pozzolanic activity i.e. the lime consuming capacity of each of these pozzolans has been evaluated by making portland cement - pozzolan paste and determining free calcium hydroxide contents after different intervals of hydration. Mechanical strengths of the above portland cement - pozzolan mixtures have also been determined. The results indicate why previous workers in this area have obtained discordant results.

Keywords: calcium hydroxides; chemical analysis; compressive strength; cracking (fracturing); fly ash; portland pozzolan cements; pozzolans; silica.

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INTRODUCTION

The pozzolanic activity of different types of pozzolans, natural, treated and synthetic, has been studied by different workers. In many of these studies the pozzolanic activity of the samples has been evaluated from the strength development characteristics of mortar or concrete mixtures made with portland cement - pozzolan mixture. Another popular method is to make pastes of $\text{Ca}(\text{OH})_2$ - pozzolan then, either to follow the rate of disappearance of $\text{Ca}(\text{OH})_2$ or to follow the rate of strength development.

Attempts have then been made to correlate the "measured" pozzolanic activity of a series of pozzolans and their physical and chemical characteristics e.g. specific surfaces, chemical analyses, different heat treatments etc. These attempts have yielded diverse results; some have reported good correlations but others none (1,2). The reasons for the above divergence are not obvious. It would be of interest if some explanations could be found for the above divergence.

Natural pozzolans or their treated products are highly porous and have high specific surface areas when measured N_2 adsorption technique. However in a chemical reaction, only the outer surfaces of the individual grains of this type of material can take part; the inner surfaces i.e.

the surfaces of the pore, are to a large extent screened off from other reactants. Recently a type of pozzolan, so called SiO_2 - fume, has been introduced in the field which does not suffer from the above disadvantage. An electron microscopic observation shows that the individual particles of silica - fume are solid spheroidal bodies of fused silica. The specific surfaces of silica fume samples vary between 20 - 30 m^2/g , and most of the individual particles are less than 0.05 μm in size. In a well mixed paste of a portland cement - silica fume mixture, there is very little of the surface of the silica fume sample which is not available for chemical reaction. It would be of interest to compare the pozzolanic activity of a silica fume sample with those of natural pozzolans of similar specific surface areas. The primary object of this work was to compare the pozzolanic activity of a sample of silica fume to that of some natural pozzolans using both $\text{Ca}(\text{OH})_2$ fixation and strength development as measures of pozzolanic activity. A secondary object was to find explanations, at least in parts, of why earlier workers had obtained such divergent results.

Materials and Experimental Techniques.

One sample of silica fume, three samples of natural pozzolans and a sample of fly ash were used in this investigation. The silica fume and fly-ash samples were used as received. The pozzolan samples were ground to pass a 74 μm size sieve. A sample of mainly quartz sand, Torre Lago sand, was also ground to the same size and was used as a reference inert powder. All the pozzolans were chemically analysed and their specific surfaces measured by N_2 adsorption technique. A single batch of portland cement was used to make portland cement - pozzolan mixtures.

300 gr. of each of the pozzolan powders were then blended for 5 min. with 1200 g. portland cement. To each blend 750 g. water was added (the over all water/solid ratio was 0.5) and mixed further for 5 min. The pastes thus produced were then cast into several 40x40x160 mm. moulds and stored in a humid atmosphere. The prisms were demoulded after 72 h. and thereafter stored in the laboratory atmosphere of 65% R.H. at 20°C until tested. At 3, 7, and 28 days the compressive strengths of the prisms were determined. Parts of the broken prisms were

ground under methyl alcohol to stop further hydration, filtered, and dried at 50°C. The dried powders were thermally analysed in a Netzsch Thermoanalyser using a heating rate of 10°C C/min. This thermoanalyser simultaneously gives TG, DTG, and DTA results. DTG and DTA were used to detect the formation of $\text{Ca}(\text{OH})_2$ and CaCO_3 . TG was used to estimate $\text{Ca}(\text{OH})_2$ and CaCO_3 quantitatively. Unhydrated mixtures were also analysed to correct for the initial contents of $\text{Ca}(\text{OH})_2$ and CaCO_3 . All the hydrated samples were examined, by means of an X ray diffractometer, for the presence and the nature of $\text{Ca}(\text{OH})_2$ crystals.

Besides main series of work the following subsidiary experiments were also performed:

- 1) 300 g. of silica fume was first mixed with 750 g. water for 5 min. To this paste 1200 g. portland cement was added (the over all water/solid ratio was 0.50) and mixed for further 5 min. The paste was cast in 40x40x160 mm. moulds as in the main series. The prisms were cured in a humid atmosphere for 72 hours and then in 65% R.H. at 20°C. The prisms were used for the visual examination only.
- 2) 300 g. silica fume, 1200 g. portland cement and 900 g. water were mixed to form a paste. The paste was treated as in serie 1 of the subsidiary series. The prisms were used for the estimation of $\text{Ca}(\text{OH})_2$ formation only. This was done to evaluate the effect of w/c ratio on the reaction rate.

Results and Discussion.

A) The chemical and physical characteristics of the materials.

- The chemical analyses of the pozzolans and the portland cement sample are shown in Table 1, which also shows the specific surface areas. All the pozzolan samples, except for Segni, have silica contents in excess of 70%. Except for the fly-ash sample, all the pozzolans have fairly high specific surface areas. It is therefore expected that except for the Segni and fly-ash samples others will be highly reactive.

B) Strength development characteristics of different mixtures.

Fig. 1 shows the strength of various mixtures at intervals up to 28 days. In discussing the strength results, it is necessary to remember that they were determined on paste prisms and as such are not directly comparable with those determined on mortar or concrete prisms.

The strength results are very unexpected. The sacro-fano pozzolan, with its second highest specific surface, gave the lowest strength at all times, even lower than those of the inert powder (Torre Lago sand). The strength results at 3 days are also unexpected. For example at this age the diatomaceous earth, which has a specific surface that is 50% higher than that of silica fume, yielded a strength about 20% lower than that of silica fume. During the sample preparation for the strength determination it was observed that some of the prisms containing highly siliceous pozzolans e.g. sacro-fano, silica fume etc. have developed cracks. These cracks appeared within 24 h. after casting even though the prisms were still in their moulds and in a humid atmosphere. Fig. 2 shows one of the cracked samples. It was then thought that the crack formation is a result of the mixing procedure used to make the prisms. To test this hypothesis the supplementary mixture No. 1 was carried out. In this case no crack was visible until the prisms were exposed to a drying atmosphere of 65% R.H.; even then the cracks were narrower but more numerous (Fig. 3), than those in the main series. It will thus appear that the time of appearance of visible cracks, their number and width depend, beside other things, on the mixing procedure. Obviously the above observations refer to prisms made with pastes; however there is no reason to believe that they are not equally applicable to mortar or concrete prisms containing pozzolans. One of the authors has, in fact, previously postulated that under certain circumstances cracks may form in mortar and concrete samples even before they are demoulded (3). The above mentioned observation may explain both the unexpected strength results of this serie as well as the discordant relationship found by different workers between the physical and chemical properties of

different pozzolans and their strength development characteristics.

C) Lime - consuming characteristics of different pozzolans.

Fig. 4 shows $\text{Ca}(\text{OH})_2$ contents of different pastes at different time intervals. Before the results could be discussed in detail, something has to be said about the way in which the results were obtained.

Combining the weight loss curves of TG and DTG, it is possible to estimate quantitatively the contents of $\text{Ca}(\text{OH})_2$ and CaCO_3 in any cement sample, either hydrated or "anhydrous". It has been observed that in many of the hydrated samples the calcium carbonate contents were higher than those of the starting materials. It has been assumed that during curing and preparation of hydrated samples for the thermal analyses, part of their $\text{Ca}(\text{OH})_2$ content have been converted to CaCO_3 . On the above assumption $\text{Ca}(\text{OH})_2$ contents of the samples were adjusted upwards to take account of the above conversion. Fig. 4 shows the corrected $\text{Ca}(\text{OH})_2$ contents of different samples. Fig. 4 shows that the curves of $\text{Ca}(\text{OH})_2$ contents can be divided into two groups. In the first group comprising Torre Lago sand, Segni and fly-ash samples, $\text{Ca}(\text{OH})_2$ contents increased regularly with time. The second group shows a dip in the $\text{Ca}(\text{OH})_2$ content vs time curves at 7 days. For a given time, the difference in $\text{Ca}(\text{OH})_2$ contents between Torre Lago and any other pozzolan is due to a reaction between $\text{Ca}(\text{OH})_2$ and the pozzolan. Fig. 4 indicates that the Segni and fly-ash samples have lower lime - fixing capacities than the other pozzolans.

The dips in the $\text{Ca}(\text{OH})_2$ content - vs time curves of the high activity pozzolans are of interest. The dip may indicate that either the pozzolan has been completely consumed by this time and the further increase in $\text{Ca}(\text{OH})_2$ is due to a continued hydration of portland cement or the rate of reaction between the pozzolan and $\text{Ca}(\text{OH})_2$ has been reduced without a compensating drop in the hydration rate of portland cement. To distinguish between the above two possibilities the 7 days old sample of the portland cement - silica fume mixture was examined by the

X-ray diffraction technique both before and after heating to 1000°C. The lines of quartz were found in the heated sample but not in the unheated sample. The formation of quartz in the heated sample indicates the presence of unreacted silica fume in the 7 day old paste. This result is also expected from the chemistry of $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system. It is not possible to react completely 27% added silica by a fraction of Ca(OH)_2 liberated from portland cement present in the mixture. This is particularly so as only a part of portland cement has been hydrated by 7 days. It is of interest to note that all the high activity pozzolans had consumed Ca(OH)_2 to the same extent; this happened in spite of their varying specific surfaces. This will indicate some other factors beside the specific surface, determine the lime - consumption rate of the pozzolans. It seems possible that the apparent drop in the lime consumption rate is due to a hindrance of material transport through a layer of initial hydration products which surround the individual grains of pozzolans.

In that case by increasing the water/solid ratio of a portland cement - pozzolan mixture the rate of cement hydration could be increased without a corresponding increase in the consumption of lime by pozzolan i.e. a mixture with a higher water/solid ratio should show a higher Ca(OH)_2 content. The second set of subsidiary work was performed to check this possibility.

In the main series the water/solid ratio was 0.50, and in the second series it was 0.60. In table 2, Ca(OH)_2 contents of both the series have been collected. From table 2 it can be seen that Ca(OH)_2 contents of the second series are higher than corresponding member of the main series. It will thus appear that the above postulated hinderence in the material transport plays an important part in leveling out the effects of the high specific surface areas of high activity pozzolans.

A reviewer has commented that sometimes with very exhaustive characterizations of pozzolans, it is possible to correlate their various properties. Our results indicate that a layer of initially formed reaction products on the pozzolan grains plays a very dominant role in their subsequent reaction with Ca(OH)_2 . If this is found to be generally true then

most of the "good correlations" would be fortuous. The reviewer also wondered if the entrapped air-voids visible on the surfaces of the samples of Fig. 2 and 3 would affect their strength or not. The surface air-voids would, of course, somewhat affect their strength. However the cracks of size visible in the figures will have catastrophic effect.

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Table 1
Chemical Analyses Of The Material Used

MATERIAL	L.O.I. %	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	CaO %	MgO %	SO ₃ %	Na ₂ O %	K ₂ O %	Sp. Surface m ² /g
SILICA FUME	2.33	94.42	0.23	0.77	0.84	0.60	0.20	0.22	0.28	20.70
DIATOMACEOUS EARTH	12.04	79.03	5.11	2.29	0.59	0.90	--	--	--	31.78
SACROFANO POZZOLAN	12.20	72.91	5.73	2.21	2.34	0.48	3.02	0.28	0.64	30.32
SEGNI POZZOLAN	4.91	46.57	18.70	9.65	11.86	4.94	--	0.74	2.52	13.40
FLY ASH	4.13	78.76	4.48	3.34	3.68	3.61	1.45	0.21	0.22	0.77
PORTLAND CEMENT	3.60	21.58	2.72	3.14	61.65	2.74	3.22	0.42	0.60	0.42

Table 2
 Calcium Hydroxide Contents Of Two Series
 Of Pastes Containing Silica Fume

TIME OF HYDRATION, DAYS	% Ca (OH) ₂ CONTENT BY THE WT. OF CEMENT	
	WATER / SOLID RATIO 0.50	WATER / SOLID RATIO 0.60
3	11.4	12.0
7	9.1	11.7
28	9.9	14.7

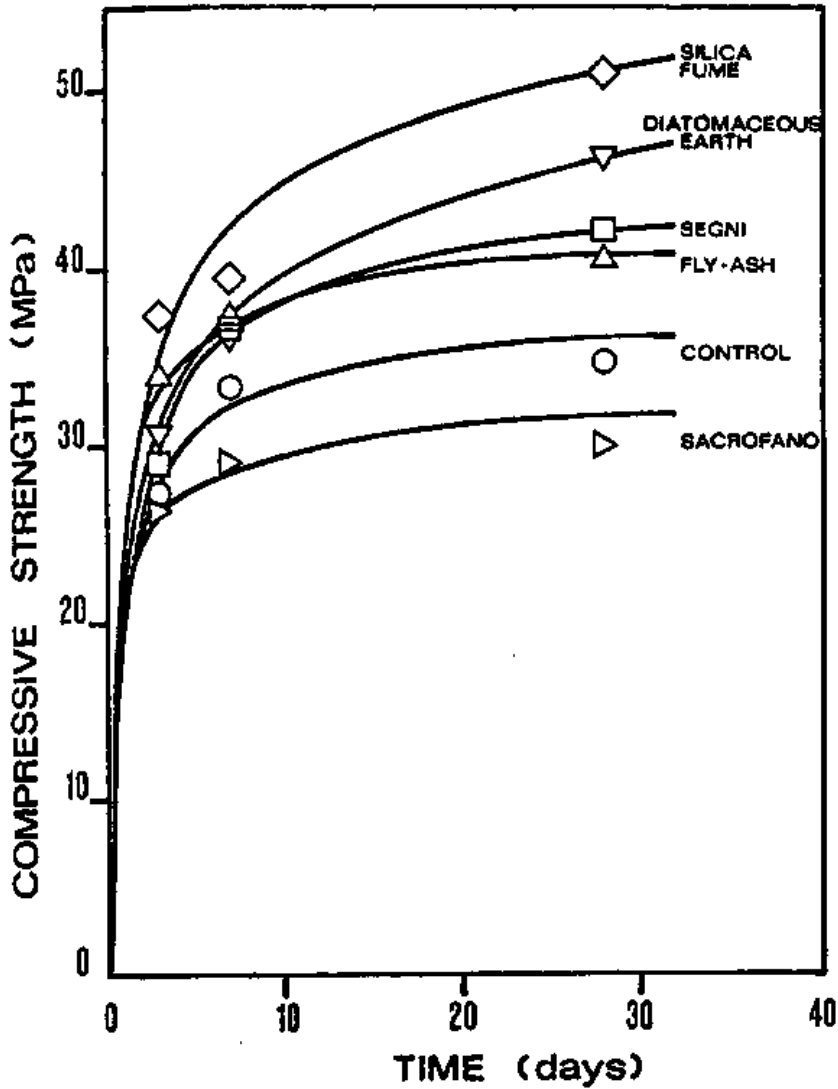


Fig. 1 Strength development characteristics of different pozzolan - cement mixtures.

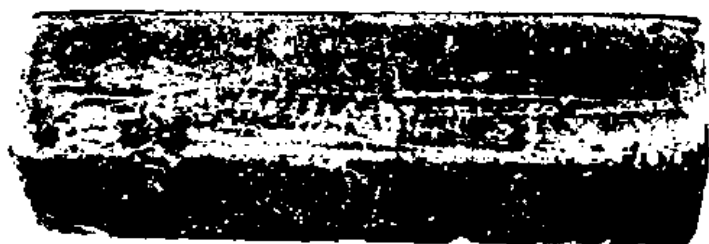


Fig. 2 Shows crack in a prism. Mixing procedure was first silica fume and cement then water. Crack appeared when the prism was still in its mould.



Fig. 3 Shows cracks in a prism. Mixing procedure was first silica fume and water then cement. The cracks appeared after the prism has been exposed to 65% R.H.

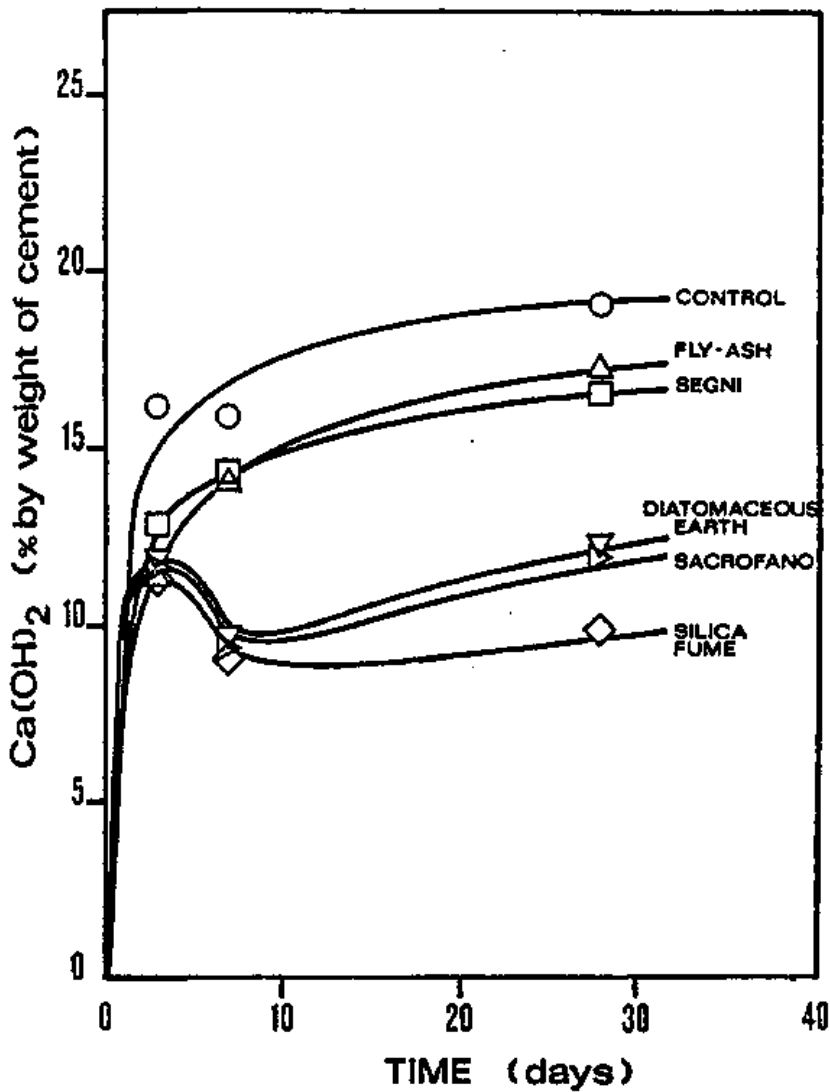


Fig. 4 Ca(OH)_2 contents of different pozzolan cement mixtures.