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INFLUENCE OF SIZE FRACTION OF PONDED ASH ON ITS POZZOLANIC ACTIVITY

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ABSTRACT

The paper examines the role of different size fractions of ponded ash, characterised in terms of their physical nature and chemical composition, on the lime-reactivity strength of ash-lime-sand mortars. The paper also presents SEM and MIP characterisation of different size fractions. The results of the investigation show the strong influence of the fine particles on their physical properties and lime-reactivity strength of mortars. Ponded ash contains both reactive, small particles and non-reactive or poorly reactive large particles, due to which it loses its overall pozzolanicity. Its use as a pozzolan in cement concrete will only be possible if the non-reactive large sized particles are separated from it. The paper concludes that the practice of wet disposal of fly ash adopted mostly in India is detrimental to the pozzolanic activity of the ash. *© 1998 Elsevier Science Ltd*

Introduction

Fly ash is now well-accepted as an ingredient of cement concrete. The fineness of a fly ash is one of the parameters which has a crucial influence on the properties of fresh and hardened mortar and concrete made with it. The particle size and crystalline to amorphous ratio of the fly ash play important roles in the reactivity towards lime, due to the pozzolanic reaction which takes place mainly on the surface of the particles (1–4).

It is generally accepted that the different size fractions obtained either directly from the various stages of collection in the ESP or separated in the laboratory using classifiers or sieves exhibit no great differences in their chemical composition, but the glassy content of the finer fraction is greater (5–8).

In India, most of the thermal power plants use a wet system for disposal of ash. The bottom ash from the boilers and the fly ash from the precipitators are mixed together and pumped off in the form of slurry to lagoons where water is drained off or recycled (9). About 1000 million tonnes of such ash, referred to as ponded ash, are currently available in India and

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more is generated every year (10). Most of the fly ash/ponded ash available in India is of the bituminous type, the exception being Neyvelli lignite ash (11).

Sharma and Krishnamoorthy (12) studied 14 Indian fly ashes collected from different thermal power plants. They grouped them as highly reactive, medium reactive, and low reactive ashes based on their mineralogical composition, morphology, glass content, and lime reactivity. Ponded ash belonged to the low reactive group. In another study, Ranganath et al. (13) investigated the influence of fineness and soluble silica content of Indian fly ashes on their lime reactivity strength at different ages and on the strength of cement concrete mixtures in which part of cement was replaced by a low reactive fly ash. They concluded that the fineness of fly ash plays an important role in the strength of mortars and concrete at early ages, via a micro-filler or a cement dispersion effect or both. At later ages, the soluble silica content of the fly ash or its pozzolanicity becomes more significant.

The influence of addition of ponded ash on the properties of cement concrete is not well known, although some investigations have shown loss of workability of fresh concrete (14) and poor early strength (15). There is a severe reluctance among engineers in India to use ponded ash in cement concrete.

Ranganath (16) has studied the characteristics of ponded ash in terms of its physical properties, chemical composition, mineralogical composition, and morphology to ascertain the variability of these within a single source, and also with those of fly ash by collecting 16 random samples at various locations and depths of a pond which contained ash 4 to 8 years old. He has reported that the variation among the samples collected from a single source is not significant in terms of physico-chemical properties. However, he has concluded that the method of disposal and process of ponding has resulted in increase in loss on ignition, decrease in alkali oxides, decrease in soluble silica content, absence of smaller particles and presence of larger number of irregular coarser particles which contribute to reduced reactivity of ponded ash in comparison with dry fly ash.

This paper examines the role of the different size fractions of the ponded ash, characterised in terms of their physical nature and chemical composition, on the lime reactivity strength of mortars and the pore refinement which occurs in ponded ash added lime mortar specimens. The principal objective of the investigation is to understand the nature of ponded ash and to arrive at the active constituents that influence the workability and development of strength of cement mortars and concrete, and to arrive at suitable recommendations in this regard.

Experimental

Out of the sixteen grab samples of ponded ash, collected randomly from the ponds of a thermal power plant located near Delhi, two representative samples (P1 and P2) were further selected for detailed investigation. Samples collected were first dried naturally in the laboratory and then stored for further test in plastic cans. Quartering was done with each sample before performing any test in order to get a representative sample and these samples were dried at 110° C for 3–4 h and stored in polythene bags. An Alpine air classifier (A 100 MZR) was used to classify ponded ash sample in to three different size fractions, namely, a fine fraction F (<20 μm), a medium fraction M (20–75 μm) and a coarse fraction C (75–150 μm).

The standard Le-Chatelier flask method was used to determine specific gravity. Fineness

TABLE 1
Physical properties of different size fractions of ponded ash.

Sample	Specific Gravity	Fineness (m^2/kg)	Lime Reactivity (10 days) (MPa)
P1	2.0	302	4.1
P1 Fraction F	2.24	427	5.3
P1 Fraction M	2.13	311	3.9
P1 Fraction C	1.93	185	1.8
P2	2.04	262	3.0
P2 Fraction F	2.19	518	5.1
P2 Fraction M	2.09	308	3.2
P2 Fraction C	1.97	194	1.6

was determined by using Blaine's air permeability method. Table 1 show the results of these tests.

Chemical analysis was carried out with oven dried samples of the different fractions of ponded ash samples (P1 and P2). Silica and combined oxides ($Al_2O_3+Fe_2O_3$) were determined using gravimetric analysis confirming to IS 1727–67 (17). Iron oxide, magnesium oxide and calcium oxide were determined by complexometric methods (largely EDTA). Alkalis were obtained by using Flame Photometer method. Soluble silica was determined after dissolution of ash; the insoluble matter including silica was separated, ashed, and the resulting oxides were fused with potassium persulphate. The silicic acid liberated from the alumino-silicate in the insoluble matter was dissolved in hot solution of NaOH but free silica (crystalline quartz) was unaffected, and was ignited separately and estimated after hydrofluorization. Alkali soluble silica was determined by using spectrophotometer method (18). The method consisted of boiling ash in 0.5 N NaOH solution for 3 min. and estimating the alkali-soluble silica by spectrophotometry. An Elico spectrophotometer (model CL-54) was employed for measuring the absorbance. Table 2 shows the results of these tests.

The x-ray diffractograms of the different fractions of ponded ash (P1) were obtained using a Rigaku D max rotating anode diffractometer. The powdered samples were pressed into the

TABLE 2
Chemical composition of different fractions of ponded ash.

Samples	LOI	SiO_2 (Total)	$A1_2O_3$	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Free Silica	Soluble Silica	Alkali Soluble Silica
P1	6.74	57.02	29.50	5.70	0.68	0.52	0.23	0.78	35.19	21.83	5.90
P1-F	5.81	58.16	28.14	5.89	0.71	0.48	0.07	0.07	34.06	24.10	6.00
P1-M	6.52	58.23	26.67	6.41	0.61	0.70	0.22	0.07	41.78	16.45	3.00
P1-C	8.44	56.37	26.54	5.55	0.76	0.92	0.33	0.11	38.16	18.21	4.15
P2	6.09	56.85	29.54	5.35	0.27	0.67	0.16	0.52	31.88	24.97	4.20
P2-F	4.44	56.18	30.24	5.62	0.68	0.78	0.08	0.69	27.66	28.52	6.00
P2-M	4.70	60.49	27.75	4.89	0.21	0.38	0.11	0.78	42.83	20.68	3.75
P2-C	8.08	59.23	26.77	3.75	0.37	0.66	0.15	0.63	35.52	23.71	4.35

TABLE 3
Lime reactivity strengths of different size fractions of ponded ash sample P1.

Size Fractions	Lime Reactivity Strength (MPa)		
	7 days	10 days	28 days
F	4.2	5.3	9.1
M	2.8	3.9	8.4
C	1.1	1.8	3.8

aluminium holder and subjected to Cu-kα (radiation between 10–55 (2 θ). A scanning speed of 5° per minute was maintained throughout.

SEM studies on different fractions of ponded ash (P1) and lime-hydrated samples of the different fractions of 7 and 28 day ages were carried out using Cambridge Stereo Scan 360. Representative ponded ash sample was placed on a specimen holder plate, compacted, and fixed with an adhesive. This plate was transferred into a sputter coater (Poloran E 5100) and a thin conducting layer of gold was deposited on the specimen surface. Gold coating was done in a vacuum of the order of 10^{-3} torr.

The broken specimens of lime hydrated mortar samples obtained after the end of test at different ages were treated with acetone, dried and preserved in a vacuum desiccator. These were mounted on the sample holder with an adhesive and were gold-coated as explained earlier for the tests.

Porosimetry studies on lime-hydrated samples of the different fractions of 7 and 28 day ages were carried out using Quantachrome, Autoscan-33 mercury intrusion porosimeter having pressure range of 227 MPa, pore radii range 7.14 μm to 0.0032 μm, and maximum intrusion volume of 2.0 cc.

Lime-Reactivity Tests

The reactivity of the different fractions of ponded ash (P1 and P2) were determined by using the lime-reactivity test of IS 1767–67. In this method, laboratory reagent grade hydrated lime and the ash are mixed with standard sand (confirming to IS 650–66) in the ratio of 1:2M:9 by weight, where, M is the ratio between specific gravity of pozzolana and specific gravity of lime. Water content of the mix was adjusted in order to get a flow of 70% (water-to-solids ratio ranged from 0.19 to 0.21). Standard 50-mm cubes were used to cast the specimens. Casting was done in two layers; each layer was tamped 25 times with a tamping rod. After completion of tamping and finishing, the moulds containing the cast specimens were kept in a temperature controlled chamber for 48 h at 27 ± 2°C temperature and at not less than 90% R.H. After 48 h, the cubes were demoulded and kept in a temperature-controlled chamber at 50°C temperature and R.H not less than 90%. At the end of a total of 10 days, the specimens were removed and tested in compression. A minimum of 3 cubes were tested and the average value of strength was reported as lime reactivity. Table 1 show the results of these tests. Also, in order to evaluate the effect of age on lime reactivity strength of different fractions, some specimens were tested in compression at the end of total of 7 and 28 days. Table 3 shows the results of these tests.

TABLE 4
Granulometric details of different size fractions of ponded ash P1 using air classifier.

Ponded ash	Fineness (Blaine's) (m^2/kg)	Residue on 45 μm sieve, %	Particles finer than 20 μm, %
FS	312	0	62
MS	290	13	53
CS	230	45	37

Current standards mostly specify fineness either in terms of specific surface area (as measured by air permeability method) or the residue on 45 μm sieve size. In order to evaluate ponded ash in terms of this later parameter, ponded ash (P1) was sieved using different maximum sizes, which resulted in three different classes of ponded ash, namely Fine Sieved (FS), Medium Sieved (MS), and Coarse Sieved (CS) having maximum size of particles of 45 μm, 75 μm, and 150 μm respectively. Table 4 shows the granulometric details of these three classes of ponded ash. Lime reactivity strengths were determined for these three classes of ponded ash at the end of 3, 7, 14, 28, and 90 days. A lower curing temperature of 40 ± 2°C and RH of 90% were maintained throughout the testing age in order to differentiate the reactivity at different ages ranging from only 3 days to a long time of 90 days. A minimum of 6 cubes were tested for each test age and class of ponded ash.

Results and Discussion

Physical Characteristics

Three characteristics namely, specific gravity, fineness, and lime-reactivity strength have shown the highest values for fraction F ponded ash having particles below 20 μm, indicating the strong influence of finer particles on these characteristics (Table 1). On the other hand, fraction C, which consisted of the most coarse particles (75–150 μm) showed low values of specific gravity, fineness, and lime reactivity strength. It is thus evident that the presence of particles above 75 μm affects adversely the physical characteristics of ponded ash. It appears that these coarse particles are what distinguishes a ponded ash from true fly ash.

Chemical Composition

Table 2 presents the results of chemical analysis of the whole ponded ash samples and their three fractions. LOI tests show that there is a larger amount of unburnt carbon in fraction C of both the samples compared to other fractions. The LOI is nearly 50% more than that in fraction F. The higher the LOI and coarser the particles, lower would be the strength. The lime reactivity results confirm the above observation (Table 1). While there is no significant variation in the different oxide compositions of the three fractions of ponded ash, fraction F has shown generally higher values of combined oxides than fractions M and C.

Fraction F showed higher (acid) soluble silica and alkali-soluble silica percentages, suggesting that it is probably more reactive. However, even fraction C contained significant

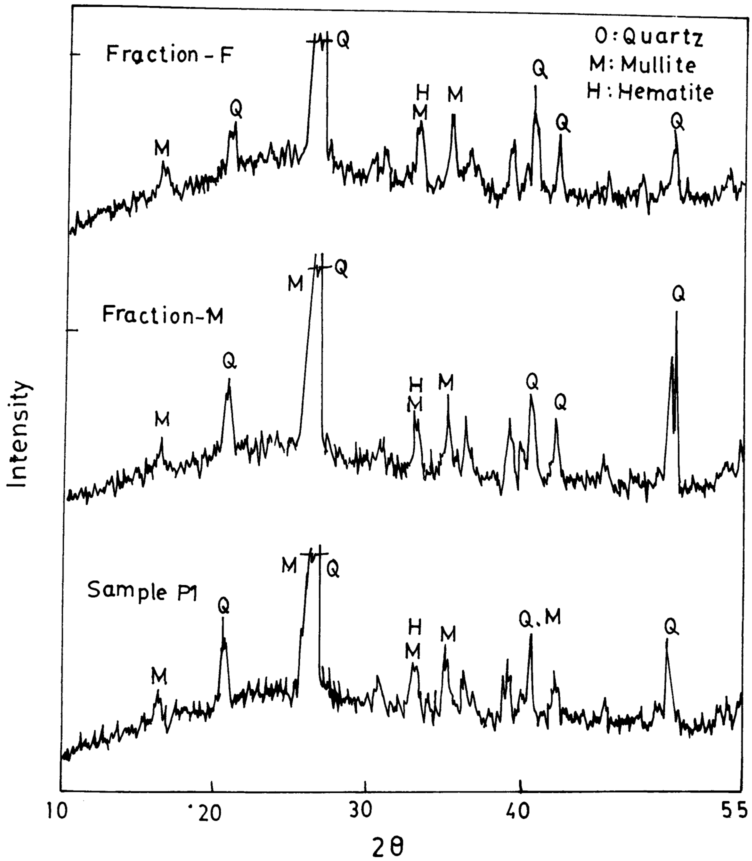

FIG. 1.
X-ray difractograms of different size fractions of ponded ash sample.

amounts of these forms of silica. The lime reactive strengths as obtained at 7 days and 10 days are not probably dependent on silica percentages, but explainable due to the differences in fineness (19). But at 28 days, the lime-reactivity strength of fraction M had shown greater gains than fraction F, suggesting a possible influence of soluble silica at later ages of continuing hydration. However, a similar large gain was not seen for fraction C up to 28 days.

Mineralogical Composition

Figure 1 shows the XRD patterns of ponded ash sample P1 and its fractions F and M. There was little change in the mineral phases of the different fractions of ponded ash as compared to the whole sample. Fraction F and fraction M ponded ashes mostly contained quartz and mullite. A close observation reveals that fraction F ponded ash had a larger base line hump at 27.5° (2θ) indicating the presence of larger glass content than that observed in fraction M and the total sample P1. This observation is supported by the fact that the soluble silica and alkali soluble silica contents of fraction F were also higher.

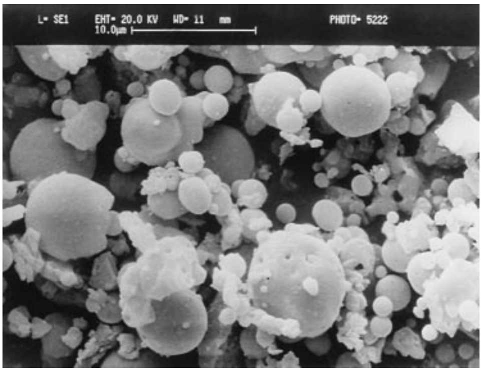

FIG. 2.
Scanning electron micrograph of fraction F.

Morphological Studies

Figures 2 through 4 show scanning electron micrographs of the different fractions of ponded ash. Figure 2 represents the fraction F. It can be observed that particle sizes of the order of 1 to 2 μm are also present in this fraction. The particles are mostly spherical having smooth surfaces. Figure 3 represents the fraction M consisting of small spherical particles along with lumps of such particles formed during the process of ponding. Figure 4 represents the fraction C. It clearly shows the large sintered particles having uneven surface and surface deposits. The high lime reactivity strength of fraction F can be attributed to the presence of smooth, spherical, small particles. Small particles are generally more glassy than large particles because of their more rapid rate of cooling (8).

The very low lime reactivity strength (1.8 MPa) of fraction C ponded ash is possibly due to the fact that large particles having uneven surfaces neither offer sufficient reaction sites for CSH formation, nor are sufficiently glassy, thus making them mostly redundant in the (lime reactivity) strength development at 10 days.

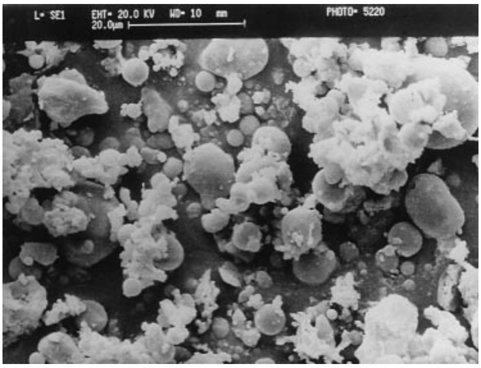

FIG. 3.
Scanning electron micrograph of fraction M.

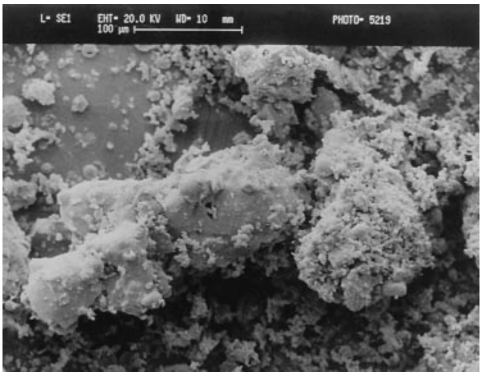

FIG. 4.
Scanning electron micrograph of fraction C.

SEM Studies on Lime-Hydrated Mortar Samples of Different Fractions of Ponded Ash

Figures 5 and 6 are SEM micrographs obtained on broken specimens of lime mortar cubes after the compression test at the end of 7 days curing for fraction F and fraction C of P1 respectively.

It can be observed that in fraction F, surface disintegration of a few particles of ponded ash had started, indicating the initiation of pozzolanic reaction. In fraction C, only traces of such reactions can be seen.

Figures 7 through 9 are SEM micrographs obtained at the end of 28 days curing of fractions F, M and C. In Figures 7 and 8, it is seen that most of the particle surfaces have disintegrated and resulted in the formation of CSH gel. It is also seen that the resulting needle-like gel structure has resulted in interlocking the adjacent particles, thereby reducing most of the large-sized pores

In Figure 9, from fraction C, no such clear disintegration of particles which results in the formation of CSH was observed. Most of the sintered particles are seen to be unreacted. The

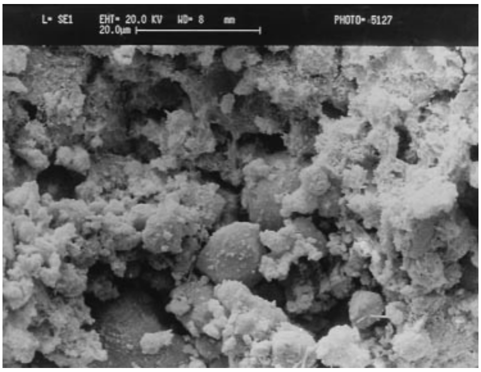

FIG. 5.
Scanning electron micrograph of lime-hydrated mortar sample of fraction F at 7 days.

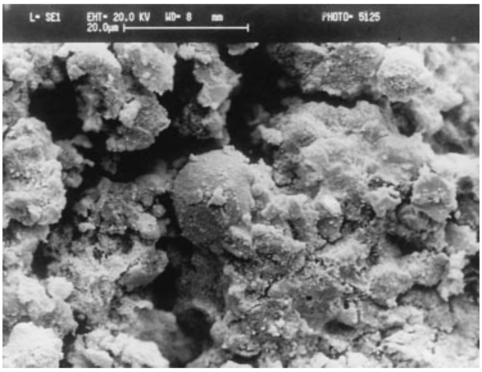

FIG. 6.
Scanning electron micrograph of lime-hydrated mortar sample of fraction C at 7 days.

interlocking of particles with CSH gel is not very evident and large-sized pores can still be seen at the age of 28 days.

Mercury Intrusion Porosimetry Studies on Lime-Hydrated Mortar Samples

Figures 10 and 11 show the percentage of pores present in a particular size range plotted against the mean pore diameter of that range for hydrated mortar samples of 7 and 28 days of the three fractions of ponded ash P1. According to Mehta (20) capillary voids represent the space not filled by the solid components of the hydrated cement paste, and their pore size ranges between 100 Å to 10,000 Å with 1000 Å as a probable mean. Further, he has stated that capillary voids larger than 500 Å are assumed to be detrimental to strength. It is seen that at 7 days of hydration (when pozzolanic reaction may have just started,) pores above 1000 Å diameter were present in relatively large amounts in all the three fractions of ponded ash. A pore-filling influence is also noted in samples of fraction F and fraction M, because the pores in the ranges of 100 Å and 1000 Å are less than those of fraction C.

At 28 days (Fig. 11), it appeared that most of the capillary pores (above 500 Å), which are

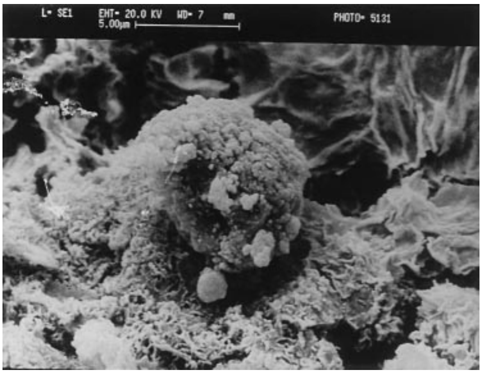

FIG. 7.
Scanning electron micrographs of lime-hydrated mortar samples of fraction F at 28 days.

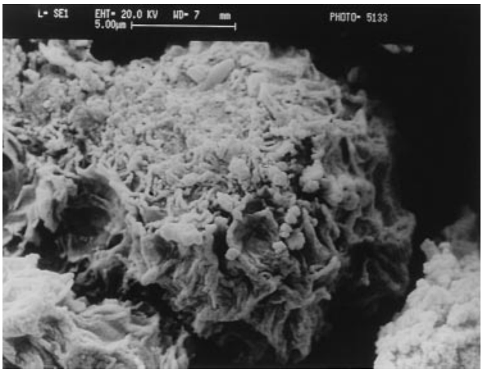

FIG. 8.
Scanning electron micrographs of lime-hydrated mortar samples of fraction M at 28 days.

assumed to be detrimental to strength have been reduced by the hydrated products indicating the influence of a pozzolanic reaction. In samples of fraction C, a significant amount of pores above 500 Å are still seen at 28 days. These larger-sized pores indicate less pozzolanic reaction of fraction C (Table 3).

Strength Development of Sieved Ponded Ash with Lime at Different Ages

It is observed that FS and MS ponded ashes exhibited higher strength than CS ponded ash at all ages (Fig. 12). The lime reactivity strength development in FS and MS ponded ashes was similar up to 14 days and, subsequently, a greater increase in strength was observed in FS ponded ash at 28 and 90 days with respect to MS ash. CS ponded ash also showed a similar trend up to 28 days but with lower lime reactivity strength, and there was little increase in strength thereafter.

The reduced lime reactivity strength of CS ponded ash at all ages can be attributed to the near absence of the very small particles, which provide nucleation sites for pozzolanic reaction. As can be seen in Table 4, only 55% of the particles are below 45 μm size in CS

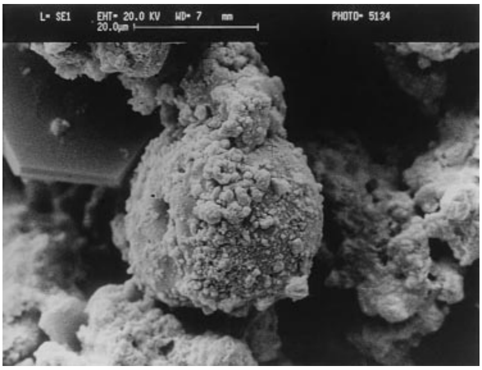

FIG. 9.
Scanning electron micrographs of lime-hydrated mortar samples of fraction C at 28 days.

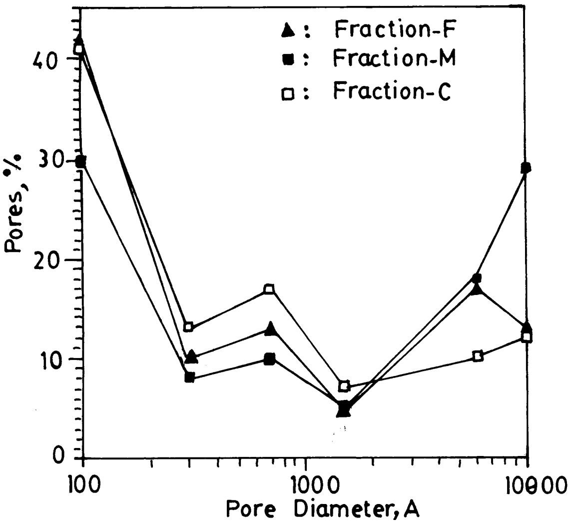

FIG. 10.
Pore size distribution of lime-hydrated mortar samples at 7 days.

ponded ash. Particles larger than 75 μm are clearly not useful for pozzolanic activity. The predominance of coarser particles in the ponded ash, its reduced alkali content, and higher values of LOI are consequences of mixing the ESP-collected fly ash with bottom ash, washing them with water and allowing them to flow randomly in lagoons. Table 5 compares these characteristics of ponded ash with fly ash from the same plant.

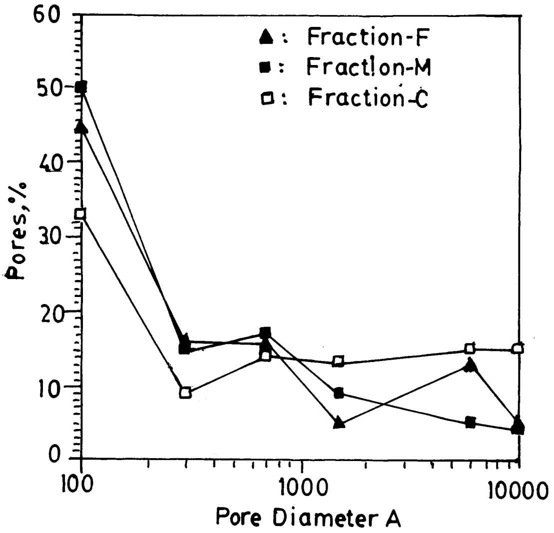

FIG. 11.
Pore size distribution of lime-hydrated mortar samples at 28 days.

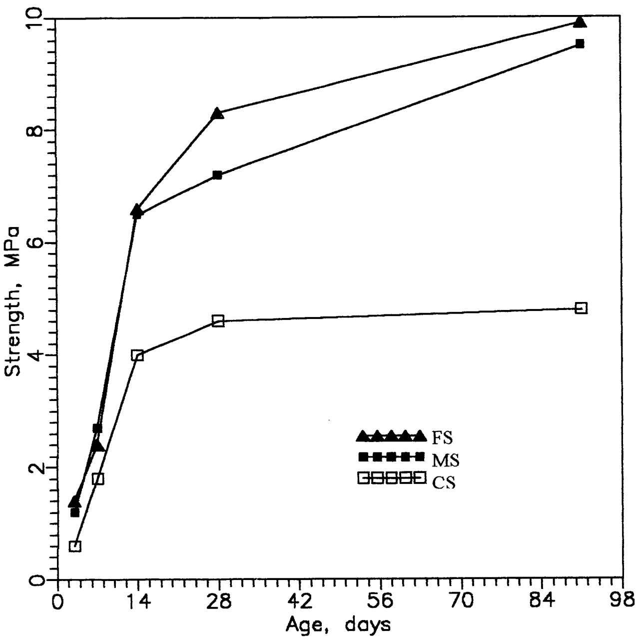

FIG. 12.
Lime reactivity strength of different classes of lime ponded ash mortar samples at different ages.

Conclusions

In general, it can be concluded that the ponded ash contains both reactive, small, particles and "non-reactive" or poorly reactive large particles. Of the various particles, only those below 75 μm (about 65% of the ponded ash) can be regarded as reactive and pozzolanic. Ponded ash in its "as disposed off" state, loses its overall pozzolanicity and hence its capacity to give strength to mortar or concrete due to the presence of large, sintered, and unburnt particles. It can only be graded as a low reactive material. Its use as a pozzolan in cement concrete will only be possible if all the nonreactive large-sized particles are separated from it. It cannot be

TABLE 5
Characteristics of ponded ash P1 as compared to dry fly ash of the same power plant.

Characteristics	Fly ash	Ponded ash
LOI (%)	5.02	6.99
Soluble silica (%)	35.56	24.70
Residue on 45 μm sieve (%)	16	45
Combined Alkalis (%)	1.59	0.78
Fineness (m^2/kg)	401	302
Lime Reactivity (MPa)	6.0	4.1

recommended strongly as a pozzolan. The method of wet disposal and mixing bottom ash/grate ash needs to be discouraged when fly ash is to be utilised as a pozzolan.

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