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ENHANCING THE POTENTIAL OF INDUSTRIAL USE OF THE INDIAN FLY ASHES THROUGH MECHANO-CHEMICAL ACTIVATION – PROSPECTS AND PROBLEMS

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Abstract

The generation of fly ash from the coal-fired thermal power stations in India is very large. At the same time, its quality is highly variable and predominantly crystalline. Since the generation is likely to touch 170 Mt in 2011-12 and about 600 Mt in 2031-32, one will have to look for newer avenues of bulk usage that have not been tried so far. This strategy requires technologies for upgradation of fly ash quality. Currently fine grinding of fly ash and cyclone classification are the technologies adopted and the product particle size reduces from a mean of 30 μm to 3-9 μm. With these particulate characteristics the properties of mortars and concrete significantly improve due to enhancement of packing density and increased number of nucleation points for cement hydration in the paste. In other words the improvement in properties is consistent with the increase in surface generation. But in Materials Science it is known that a decrease in the size of the crystals below some threshold value may result in a disproportionately large change of properties. This observation has been made profusely in the context of nanomaterials with mean size of particles below 100 nm. But there is always a region in the submicrocrystalline field of materials going up to 300 nm.

This paper addresses the issues pertaining to the prospects of finding a threshold value for the Indian fly ash particles which may lead to large change of properties, which, in turn, may unfold possibilities of newer bulk applications of fly ash by virtue of such mechano-chemical activation.

Introduction

It is well-known that in India the generation of electricity is overwhelmingly dependent on the combustion of coal in thermal power plants and the process generally generates about 20 per cent bottom ash and 80 per cent fly ash. The quantum and characteristics of the above process wastes are strongly influenced by the coal quality, the milling systems, the design and operation of boilers and the collection system of the ashes, and consequently may differ significantly from plant to plant and even within a single plant. The trends of generation and utilization of fly ash in India earlier, now and later are shown in Table 1.

Table 1. Fly ash generation and utilization in India

Year	Generation (G) Mt	Utilisation, Mt (% of G)	Remarks
1993-94	40	1.2 (3%)	Commencement of the National Fly Ash Mission
2004-05	112	42 (38%)	Fly Ash Mission continuing as Fly Ash Utilisation Programme
2006-07	130	60 (46%)	Same as above
2011-12	170	170 (100%)	Total utilization projected
2031-32	600	?	No consolidated utilization plans available

It is obvious from Table 1 that the rate of generation of fly ash has so far been overtaking the rate of enhancement of gainful utilization. In the next three or four years the target of total utilization of fly ash likely to be generated is a daunting task by itself. If one looks at the likely generation of fly ash in India, say about two decades from now, it is gigantic in volume and its utilization programme will have to be far more challenging than what is perceived to-day. It is also obvious that no niche utilization strategy would work and one will have to look for newer avenues of bulk usage.

In this context it is relevant to look at the current broad pattern of bulk use of fly ash as depicted in Fig 1.

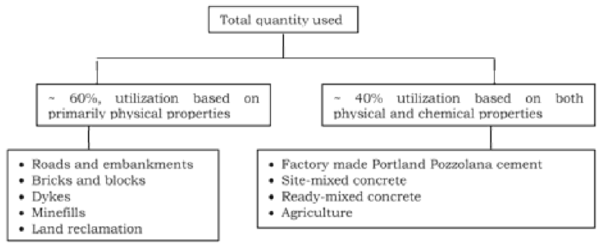

Figure 1. Current broad pattern of bulk utilization of fly ash

The major impediments in enhancing the application potential of the Indian fly ashes even in the above segments can be seen as follows:

- Inter-source and intra-source variability
- Wide distribution of particle size
- High order of crystallinity
- Wide fluctuation of specific surface area

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Endeavors being made to overcome the above impediments in order to enhance the use of fly ash in the aforesaid areas and the possibilities of opening up newer fields of applications are discussed in this article. In the context of the new applications such as substitution of silica fume, polymer fillers, paint and enamel extenders, etc., the scope of application of mechano-chemical activation seems quite potential. The technical feasibility of this approach has been looked into in this paper.

Technological Approaches for Enhancing the Use of Fly Ash in Cement and Concrete Industry

Illustrative Quality Parameters and Current Usage

It is known that the fly ash is separated from the gases generally with the help of multi-field electrostatic precipitators. The pattern of collection in each field is shown in Table 2

Table 2. Field-wise collection of fly ash in electrostatic precipitators

Fields	Approximate proportions of collection (%)	Typical Specific Surface Area (m^2/kg)
I	60	250
II	23	450
III	10	600
IV	3	700
V	2	800
VI	2	850

Since the final collection hopper contains materials of all the fields, the specific surface areas of the fly ashes as received at the user end are on the coarser side and quite variable as shown in Fig. 2.

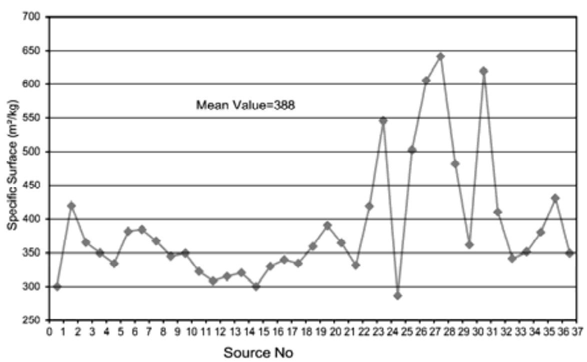

Figure 2. Variations observed in the specific surface area of fly ashes of different sources

Apart from the specific surface area or fineness, the reactivity of fly ashes is also dependent on the mineral phases and glass content in them. It has been widely observed that the Indian fly ashes, which are of predominantly low-lime C-class variety, are highly crystalline, compared to many other countries as shown in Table 3.

Table 3. Comparative phase composition of the Indian fly ashes

Phases	Proportions in fly ashes from (%)				
	UK+	USA+	Canada*	Japan+	India*
Quartz	1 - 6.5	0 - 40	5	5 - 12	11 - 31
Mullite	9 - 35	0 - 16	6	8 - 18	9 - 31
Magnetite	<5	0 - 30	0.3	-	0.1 - 1
Haematite	<5	1 - 8	-	0.5 - 5	-
Glass	50 - 90	50 - 90	82	69 - 84	47 - 60

+ Ref. [1]
* Ref. [2]

The crystallinity of the India fly ashes can be easily observed from the XRD patterns (Fig. 3) [2]. With these intrinsic characteristics the fly ashes show high variability in lime reactivity (Fig. 4) which is a basic test of suitability of a fly ash for use in cement and concrete.

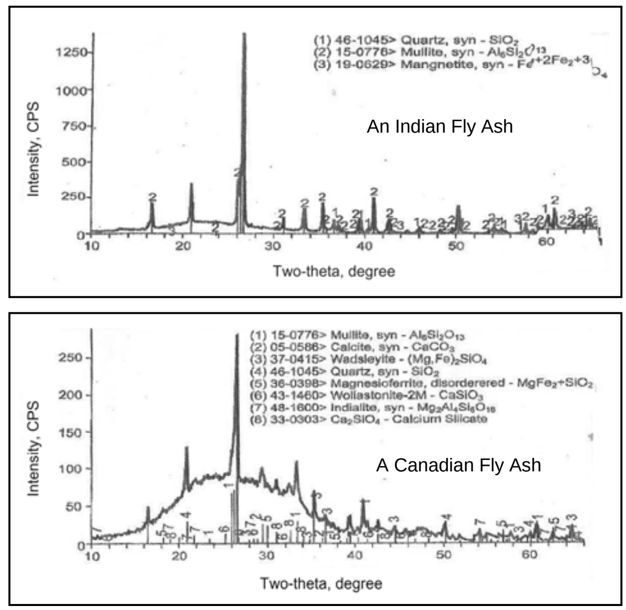

Figure 3. Comparison of XRD patterns of an Indian and a Canadian fly ash with varying crystallinity

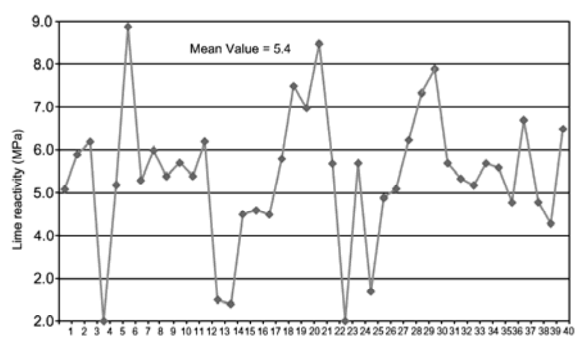

Figure 4.Variations in the lime reactivity values of fly ashes of different sources

Notwithstanding these limitations the present consumption of fly ash by the cement industry alone is estimated at more than 25 million tonnes per year, if it is presumed that the production of Portland Pozzolana Cement is about 100 million tonnes per year with fly ash incorporation of at least 25 per cent.

Looking at the future and based on the forecasts made for the industry, it is estimated that the production of Portland Pozzolana Cement by the year 2011-12 may exceed 180 million tonnes per year in the total cement production of 263 million tonnes and if the absorption of fly ash can be enhanced all over the industry to the present permissible limit of 35 per cent, the consumption of fly ash by the cement industry alone may rise to at least about 60 million tonnes per year. The realization of this large potential of gainful utilization of fly ash is dependent, to a large extent, on enhancing their pozzolanicity or reactivity by adopting newer technologies.

Technology of Fly Ash Classification

One of the most prevalent technologies adopted by the cement industry is the classification of fly ash by the high-efficiency cyclone separators into different narrow-range particle size fractions (Fig .5).

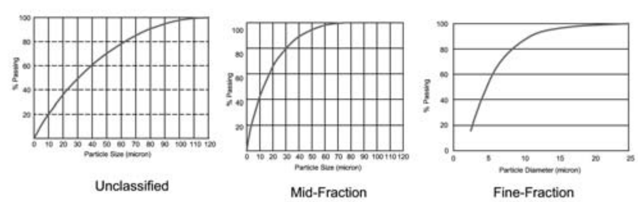

Figure 5. The particle size distribution curves of a classified fly ash

In a specific study [3] pertaining to the improvement in properties of the classified fine fly ash, it was observed that there was significant difference in its particle size and distribution as compared to the unprocessed fly ash (Table 4). When this classified fine fraction was used in mortar, the properties were significantly improved due to the enhancement of the packing density of the freshly mixed mortar (Fig. 6). This densification of the hydrated cement paste was obviously due to the increased number of nucleation points for cement hydration by the high fine particulate content.

Table 4. Differences effected in particle size distribution by classification

Fly Ash	Mean size, µm			Volume, above (%)		
	d (v, 0.1)	d (v,0.5)	d(v,0.9)	10 µm	20 µm	45 µm
Unprocessed	1.9	19.2	76.8	64.7	49.0	24.2
Processed fine fraction	0.9	2.0	4.5	0.2	0.0	0.0

In another study [4] more focused on the differences in fluidity of cement paste, mortar and concrete caused by classified fly ashes of different size ranges, one could observe certain differences in the characteristics of fly ashes having different levels of fineness (Table 5).

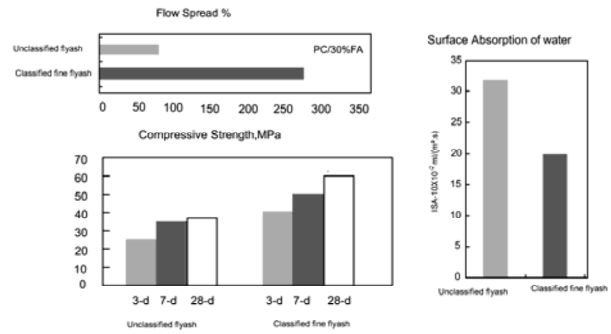

Figure 6. Improvement in mortar properties due to incorporation of classified fine fly ash

Table 5. Properties of classified fly ashes as an illustration

	Properties	Fly ash fractions		
		Coarse	Finer – 1	Finer – 2
1.	Specific gravity (g/cm^3)	2.111	2.256	2.256
2.	Blaine surface (m^2/kg)	370	761	819
3.	BET (m^2/kg)	-	1560	2220
4.	Laser diffraction (m^2/kg)	1514	2819	3185
5.	Mean particle size (µm)	27.16	9.31	6.05
6.	Zeta potential (mv)	- 27.35	- 35.57	- 80.67

From the above table it is evident that the fineness values measured by three different techniques cannot be correlated with each other. At the same time, it appears from the comparison of fine fly ash 1 and 2 that when there was a reduction of mean particle size by 35% from sample 1 to sample 2, the BET surface correspondingly showed on increase of about 42%, whereas the Blaine and Laser values showed changes of only 7.6% and 13% respectively. Thus, for characterizing the high fine fly ashes, the BET surface measurement appears more reliable than the other ones, although the Blaine surface is being widely used at present.

The effects of the replacement of cement by the fine classified fly ash on the mortar/concrete properties are shown in Fig. 7 and 8. Water demand in mortar preparation decreases steeply with increase in fineness upto 20% replacement and thereafter there is slowing down of the rate of water demand or even increase with higher levels of replacement of cement by fly ash. However, in concrete the water reducing effects were seen to be more at higher fineness and higher levels of cement replacement by fly ash.

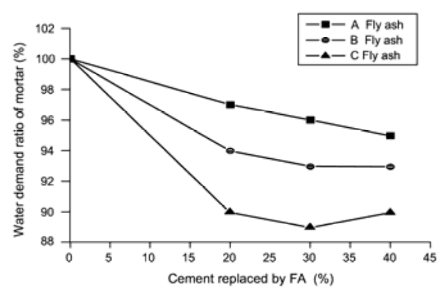

Figure 7. Effect of FA replacement levels and fineness on water demand ratio of mortar

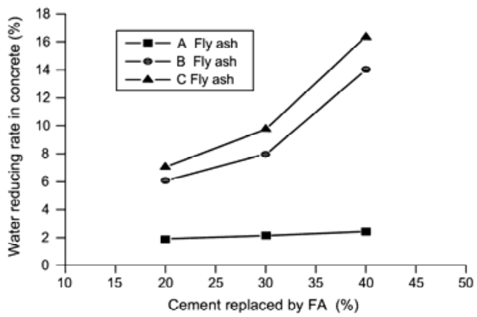

Figure 8. Effect of FA replacement levels and fineness on water reducing rate

In all the above examples, one feature that comes out quite prominently is that the fineness level of fly ashes has improving effects on various properties of the products in which they are used but the effects can not be seen to be of the level of mechano-chemical activation which is often caused and characterized by the presence of very large number of surface molecules or atoms, as compared with the molecules or atoms in the bulk of the materials. This is perhaps due to the fact that the mean particle size of classified fly ashes still stays in the micron range.

The same reason might be valid when one attempts to compare the performance of classified fine fly ash with silica fume, claimed to be a very effective mineral admixture to make impermeable concrete. Some comparative results are presented in Table 6 [5].

Table 6. Performance comparison of classified fine fly ash and silica fume in concrete

	Composition & properties	Control concrete	Fine fly ash incorporated concrete	Silica fume incorporated concrete
1	Mean particle size, d_{50}, µm, of the mineral admixture	-	3	~ 0.1
2	Addition of mineral admixture (%)	-	10	10
3	Water/cement ratio	0.40	0.40	0.40
4	Cement content in concrete, kg/m^3	400	357	356
5	Slump, mm	100	80	80
6	Compressive strength, MPa			
	7 – day	56.2	54.5	71.0
	28-day	67.9	68.7	80.7
7	Rapid Cl^- permeability, coulomb			
	7 – day	2922	1083	429
	28 - day	2340	758	297

From Table 6, it is evident that there is significant difference in the performance of classified fly ash and silica fume in achieving the impermeability level in concrete. Therefore, the real search for technologies to chemically activate fly ash has to continue.

Ultrafine Grinding of Fly Ash to Make Large Change of Properties

Having not achieved the true results of chemical activation by the classification process, various milling options in lab and pilot scale have been and are being explored by the Indian cement industry. One of the objectives is the possibility of introducing elastic, plastic and shear deformations to fly ash particles, leading to their fracture and amorphization. The options examined include various mechanical milling systems, as discussed below.

Status of Mechanical Milling

It is wellknown that mechanical milling is the most productive method of producing large quantities of nanocrystalline powders of different types of materials such as metals, alloys, intermetallics, ceramics and composites. Milling and mechanical alloying are carried out using high-energy planetary, ball and vibration mills, where the mean size of the produced powders may vary from 200 to 5-10 nm. Some examples as furnished in [6] are reproduced here. When milling β–FeB in a ball mill, it is possible to produce a powder of α–FeB with a mean crystallite size of about 8 nm. Mechanical treatment of barium titanate $BaTiO_3$ in a planetary mill can produce nanocrystalline powder with a mean particle size of 5-25 nm. Mechanical alloying of the powders of borides, carbides, silicides, oxides and sulfides of transition metals has been carried out by the “explosive” method in vibration mills. The powders of the transition metal nitrides with a particle size of several nanometers are synthesized by milling powders in a vibromill in a nitrogen atmosphere. Mechano-chemical synthesis in ball mills of nanocrystalline TiC, ZrC, VC and NbC from powder mixtures of metal and carbon has also been reported. Although carbides form after 4-12 h milling, the particle size develops after 48 h milling to a size range of 7±1 nm. Ball milling can be used to make a variety of new carbon types including carbon nanotubes.

Unlike the above experience, the mechanical milling of fly ash has given a different trend of grindability. The typical results of grinding in a small ball mill are shown in Table 7.

Table 7. Results of extended ball milling of an Indian fly ash

Grinding time, h	Blaine surface, m^2/kg	Density g/cm^3	Lime reactivity, MPa
0	300	2.10	5.8
1	490	2.30	7.0
2	550	2.35	-
3	630	2.39	-
4	710	2.42	9.5
5	780	2.48	-

By and large, the comparative results of fly ash grinding in the labscale ball mills and twin-tube vibratory mills in dry mode as well as in the attrition mills in wet mode can be summarized as given in Table 8.

From the table it is evident that in the case of dry milling the vibratory mills displayed significantly lower milling time and

Table 8. Lab-scale grinding trials of the Indian fly ashes by the different milling systems

Mill system and mode of milling	Milling time, min	Factor of increase in Blaine surface	Reduction ratio of Median particle size	Factor of increase in Lime Reactivity
Ball mill (Dry)	300-360	3.0 – 3.5	3.0 – 3.8	2.0 – 3.0
Vibratory mill (Dry)	50-60	3.5 – 3.8	5.0 – 6.0	2.5 – 3.0
Attrition mill (Wet)	30-40	3.5 – 4.0	8 - 10	2.5 – 3.0

better product characteristics. But the attrition mill in wet mode showed even better performance. However, the average particle sizes of fly ashes ground in different milling systems ranged from 3.0 to 9.0 µm and the enhancement of fly ash reactivity was, for all particle purposes, proportional to the levels of fineness achieved. No discontinuity or sharp change in the product reactivity was observed. The XRD pattern and scanning electron micrographs did not show any noticeable difference. All these observations, prima facie, indicated the absence of any role of milling mechanisms in the mechanical activation per se. Increase in the specific surface area due to milling was the only factor to enhance the reactivity of fly ash. Since vibro-milling and attrition milling showed some potential to reduce milling time and consequently the energy consumption, the scale-up possibilities of these systems were examined.

Scale-Up Evaluation of the New Milling Systems

Two specific attempts have been made in this regard.

A pilot vibratory mill of 1.5 tph rated thoughput with twin tube of 600 mmΦ x 3500 mm length has been installed in an Indian cement plant. The rated mill drive of 90 kW has been provided with 62% volumetric filling of cylpebs of 30x30 mm, 25x25 mm and 20x20 mm sizes. For this model the problems encountered so far have been the non-achievement of rated throughput, desired reduction ratio and the expected specific power consumption. In all the three counts the upscaled version is yet to perform.

Another endeavour has been with a tower mill, as a variant of the attrition mill but in dry mode, keeping in view the fact that the tower mills or vertimills of throughput of upto 100 tph were in industrial use essentially in wet mode. The pilot-scale trial runs with the Indian fly ashes having feed particle size range of 1-100 µm did not yield the d_{50} value of even 10 µm with specific power consumption of up to 110 kWh/t of fly ash. Use of coarse media (6 mm), low tip velocity of the stirrer (3 m/s) and dry mode were considered responsible for not achieving the expected performance.

The other milling systems like the stirred mills in general and more particularly the horizontal IsaMill type systems merit some attention, as the power intensity in the latter mills is quite high (say, 300-1000 kW/m^3 compared to 50-100 kW/m^3 in vertical Sala mills). However, for metallic ores the particle size reduction below 5-10 µm has not been reported. Further, the milling being intrinsically wet, the drying issue becomes critical for fly ashes.

Search for Threshold Fineness of Fly Ash for Mechano-Chemical Activation

From the preceding discourse it is evident that with the known technologies of fine grinding and high-efficiency cyclone classifications the particle size of fly ashes remains above 1 and below 10 µm in general (Fig. 9) [6], which is much coarser than the field designated as "submicrocystalline" having mean grain size in the range of 300 to 40 nm. In Materials Science it is generally observed that a decrease in the size of the crystals below some threshold value results in a large change of properties. These effects occur, as it is believed in to-days Nanoscience, when the mean size of crystalline grains does not exceed 100 nm. Whether this threshold value is true for the fly ashes in general and the highly crystalline Indian fly ashes in particular is an issue to be resolved. However, the performance of silica fume having mean particle size of 100 nm in general (Table 6) has given an indication that the quantum jump in the properties of the Indian fly ashes can not be expected as long as the mean particle size remains above 1 µm, which has been seen so far as the size reduction limit of the known and potentially upscaleable fine grinding and classification technologies.

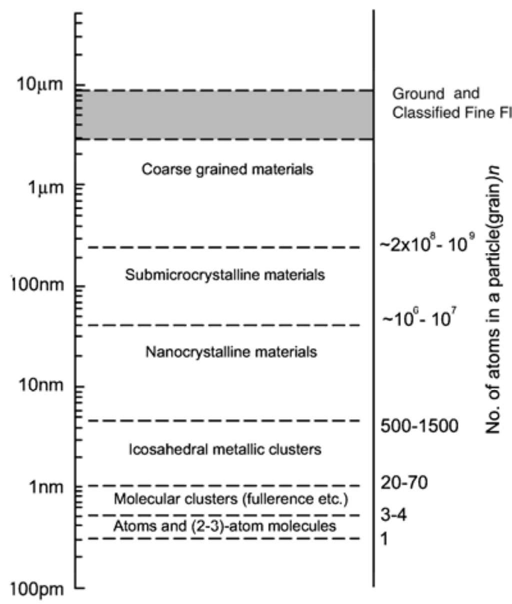

Figure 9. Scale classifying the materials on the basis of their particle size

In search of the threshold particle size of fly ash to effect large change in properties it may be worthwhile to compare with certain other mineral admixtures and fillers used in the cement and concrete industry in terms of their particle characteristics and reactivity.

As already mentioned, silica fume is an effective mineral admixture. Depending on the source, the SiO_2 content may vary between 94-98 % in the case of silicon metal and between 86-90 % in the case of alloys. The average particle size in about 100-150 nm and the BET specific surface area is 15-25 m^2/g [7]. The effect of the use of silica fume in concrete has already been shown in Table 6.

Compared to silica fume, the performance of aqueous silica colloid suspensions (known as cembinder) is also worth-noting [8]. This admixture contains silica colloid particles in an amount of 8-60% by weight of the solution. The specific surface area of the particles is in the range of 50-200 m^2/g and the mean size of the particles ranges from 5 to 200 nm. It is reported that 4% Silica colloid consumed 60% more calcium hydroxide than 4% silica fume in the same hydration period of 7 days. Even in one day the silica colloid reacted more with calcium hydroxide than silica fume. One may therefore observe that the high reactivity of the colloid silica is on account of its nanometric particle size and purity.

Another important concrete admixture is metakaolin (mk) containing 51-55% SiO_2 and 40-45% Al_2O_3. The BET surface area is in the range of 14-22 m^2/g with particle sizes of 60 to 90% under 2 μm and less than 15% above 5 μm. This type of admixture shows a pozzolanic reactivity of about 840 mg CaO g^{-1} mk by the Chapelle test [9]. This metakaolin with similar particulate dimensions as of fly ash seems to behave in a fairly comparable manner.

Finally it may be relevant to compare the behaviour of fine ground limestone filler in cement. It is generally integround with clinker and because of its softness becomes more fine than the latter. For an overall specific surface area (Blaine) of 420 m^2/kg, 50% of the filler can be below 700 nm, compared with 3 μm of clinker. Because of the fineness, it accelerates the hydration of the alite and aluminate phases. Chemically it reacts with the aluminate phase, producing a hydrated carboaluminate phase, thus competing with the gypsum [7].

From the above examples one may observe that the submicrocrystalline materials behave quite differently from materials coarser than 300 nm as depicted in Fig. 9. Hence, it is certainly worth looking at the feasibility of bringing down the mean particle size of the crystalline fly ashes in the submicrocrystalline range and observe the corresponding improvement in reactivity by the Chapplle test or by the standard lime reactivity test. Using this as the reference point, an exercise needs to be undertaken to optimize the top size of the ultrafine fly ash particles along with their size distribution pattern so as to achieve the tangible benefits of mechano-chemical activation. The main scope of this optimization exercise is to answer the following questions for the crystalline fly ashes :

(a) Is there a sharp and distinctive boundary between the bulk and the submicrocrystalline states ?

(b) Is there some critical grain size below which the characteristic properties of submicrocrystalline or even nanocrystalline material become observable and above which the material behaves as a bulk one ? In other words one will have to examine if the transition from the bulk to nanocrystalline state is the phase transformation of the first order for the fly ashes under consideration from the thermodynamic viewpoint. In this exercise the development of an appropriate conversion technology for the Indian fly ashes from the bulk to submicrocrystalline or nanocrystalline state will turn out to be the most important step.

Concluding Remarks

The fly ash generated by the coal-fired thermal power stations in India has already been recognized as a material resource. While at present about half of the fly ash generated in the country is gainfully utilized, the problem of utilizing about 170 Mt of fly ash in totality by 2011-12 appears a challenging task. The magnitude of this task will grow manifold in the next couple of decades when the generation of fly ash may touch 600 Mt.

The current pattern of bulk utilization of fly ash is strongly dependent on the use of fly ash by the cement and concrete industry but it excludes such applications as polymer fillers, paint or enamel extenders, substitution of silica fume, etc. In order to find out the newer fields of application as well as to fully avail of the scope of utilization that the cement and concrete industry presents, the properties of the Indian fly ashes that are highly crystalline, relatively coarse and widely variable, need to be substantially improved.

Presently, this improvement in properties is being partially achieved by fine grinding and high-efficiency cyclone separation technologies. Notwithstanding the adoption of such technologies, the size of fly ash particles remains in the range of 3 – 9 μm. In other words the known and currently practised technologies cannot yield particles in the submicrocrystalline range, which is defined as 300 to 400 nm. Consequently, even with fine grinding and classification the fly ash properties do not show such changes as demonstrated by the submicrocrystalline or nanocrystalline materials. The difference between the properties of small particles and properties of bulk materials is known and has been utilized in aerosols, pigments, glass coloured by colloidal metal particles etc. A similar approach is, therefore, called for in maximizing the enhancement of properties of fly ashes.

It has been observed that by reducing the mean particle size of the fly ashes from 30 μm to below 10 μm, substantial improvement in the flow and strength properties of mortars and concrete are achieved but the enhancement of properties corresponding to further reduction of fly ash particle size to even 3-5 μm is either incommensurate or inconsistent.

However, when the behaviour of silica fume, silica colloid or submicron-sized limestone fillers in cement and concrete is compared with that of finely ground and classified fly ash, it becomes evident that if the mean particle size of fly ashes is reduced to submicrocrystalline level, there are chances of significantly enhancing the reactivity of the material. This calls for the development and adoption of appropriate ultrafine grinding and classification technologies.

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