Quantitative Morphological Characterization of Cement Particles of different milling systems and its relationship with physical properties of Cements

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Abstract:

The morphological characteristics of cement particles can be quantified by parameters like Length, Breadth, Area, Perimeter, Aspect ratio, Roundness, Fullness ratio & Compactness. However, quantitative measures of shape descriptors like roundness/form factor [$4 \pi A/P^2$], fullness ratio & shape factor [$(P^2/A)-4\pi$] are not commonly employed for morphological characterization unlike remaining parameters.

In the present study three different varieties of cements namely Ordinary Portland Cement, Portland Slag Cement & Portland Pozzolana Cement drawn from different milling systems, i.e. close circuit Ball Mill, Vertical Roller Mill & hybrid systems consisting of Roll Press & Ball Mill have been analyzed using digitized images, in order to explore the effect of above shape descriptors on cement properties. The paper endeavours to unfold the relationship and significance of these morphological parameters with respect to functional characteristics of cements.

1.0 Introduction:

For a long time, ball mills have commonly been used in cement industries for comminution of clinker and additives. But since ball mills operate with lower energy efficiencies, most of the input energy is wasted in heat dissipation. During the last decade, various other grinding techniques have been commercialized/ developed for clinker grinding which results in considerably decreased energy consumption due to their higher grinding efficiencies. New technologies notably accepted in cement industries for clinker grinding include Vertical Roller Mills, High Pressure Grinding Roll Presses and combination of Roll Press and ball mills [1]. These different mills can be generally classified with respect to the main stress that acts on the particles: compression, shear, attrition, impact, and internal forces. However, it is often difficult to discriminate these types of stresses because a combination of at least two of them tend to act simultaneously in the given machine. Moreover, three modes of fragmentation are usually defined namely: abrasion, chipping and massive breakage, which more or less occur simultaneously during a comminution process. Therefore depending upon the comminution mechanism, particular mode of breakage is expected to affect the shape of product particles [2-7]. Generally massive fracture is known to result in highly irregular particles with sharp edges. Attrition of particles, by surface erosion or chipping at edges or corners on the other hand, is more likely to cause rounding of particles although the small fragments removed may be quite irregular in shape. Since there are normally distributions of particle sizes and applied stresses, it is reasonable to expect a distribution of product shapes. Therefore it is important to know the effects of the milling system (i.e. method of breakage) on the particle shape mix and whether the shape mixes of the product particles change with particle size.

Since last couple of years the importance of particle shape is being recognized increasingly due to their effects on flowability, abrasivity, compactability, reactivity, slurry rheology, etc. For particles produced by comminution, shape may be determined by material characteristics such as crystal cleavage and by the nature of the breakage process involved. Thus although it is generally accepted that different modes of comminution can lead to changes in cement particle shape, relatively few attempts to quantify these effects have been reported. Furthermore, largely due to the lack of widely accepted measures of particle shape, understanding about evolution of cement particle shape in grinding processes is far from satisfactory.

In the present paper, an attempt is made to characterize particle shapes of various cements namely Ordinary Portland Cement (OPC), Portland Pozzolana Cement (PPC) and Portland Slag Cement (PSC) for different milling systems and examine their effect on physical properties of cements, if any. The milling systems examined for particle shape evolution include Ball Mill, Roll Press followed by Ball Mill (Combi-grinding) and Vertical Roller Mill.

2.0 Materials & Methods:

Representative product samples for OPC, PPC and PSC were taken from various commercial milling circuits as indicated in Table 1.

Table 1: Description of samples & milling circuit systems used in the study

Sr.	Sample	Description
1	OPC_1	Closed circuit Vertical Roller Mill (VRM)
2	OPC_2	Closed circuit Roll Press (RP) with high efficiency classifier
3	OPC_3	Closed circuit Ball Mill (BM) with high efficiency classifier
4	PSC_1	Separate grinding of clinker and slag in VRM followed by Paddle mixer
5	PSC_2	Mixing of ground slag (in RP) & ground clinker (in BM)
6	PPC_1	Closed circuit BM with high efficiency classifier
7	PPC_2	Pre-grinding using RP followed by finished grinding using BM with high efficiency classifier
8	Fly ash (FA)	As used in case of PPC

Particle size distributions of all the samples were determined using CILAS® Laser Particle size analyzer. For doing shape analysis of particles, samples were subjected to sieving in five different size classes namely +106μm, (-106+90) μm, (-90+75) μm, (-75+45) μm & -45 μm respectively. All the collected particles in the respective classes were then dispersed ultrasonically and consequently subjected to Optical microscopy (James Swift, UK) having Image analyzer (Leica, UK) facility for capturing images. The captured images were then processed digitally for arriving at various shape descriptors characterizing the particles. For each size class around 500 particles were examined for arriving at statistically representative shape parameter distributions. Thus specific shape parameter distribution for each product comprises around 2500 particles. Further, morphological character of particles in all the size classes were also determined using Environmental Scanning Electron Microscopy (EVO40, Carl Zeiss, UK). Other physical properties of various cements such as normal consistency, setting times, Blaine surface area, Specific gravity, strength, etc were determined using Indian standard methods (IS-4031). Flowability of cement was determined using mini slump method at water cement ratio of 0.5. Similarly chemical analyses of all the samples considered in the study were carried out using standard methods (IS-4032) and are reported in Table 2.

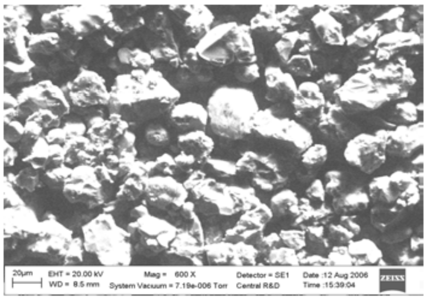
Table 2: Chemical analysis of the samples used in the studies

	OPC_1	OPC_2	OPC_3	PSC_1	PSC_2	PPC_1	PPC_2	FA
SiO_2	19.6	21.70	21.30	26.9	27.00	31.49	31.73	60.14
Al_2O_3	5.2	4.79	4.84	14.2	12.50	9.69	9.77	23.78
Fe_2O_3	3.3	4.99	5.11	2.5	2.25	4.87	4.99	4.1
CaO	61.5	62.63	62.09	44.8	46.50	47.06	48.68	1.42
MgO	3.4	1.07	1.09	6.5	6.86	1.01	1.21	0.28
K_2O	1.11	0.48	0.45	0.8	0.9	0.61	0.62	0.70
Na_2O	0.04	0.21	0.20	0.07	0.25	0.15	0.15	0.31
SO_3	2.9	2.84	2.96	1.8	1.06	2.46	2.54	0.46

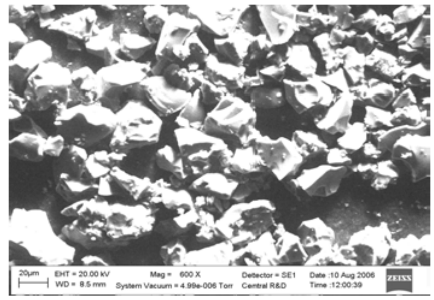
3.0 Results & Discussions:

3.1 Size & shape analysis:

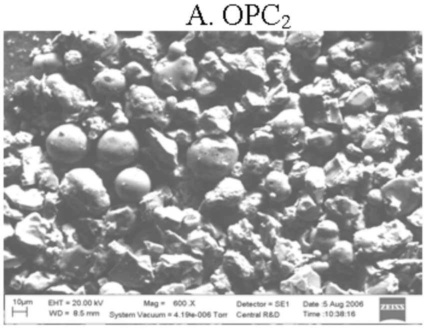
Several different approaches to the analysis of the particle shape have been described in literature. One of the methods includes Fourier analysis of the vector polar co-ordinates of the particles leading to Fourier coefficients and their relations to different shapes establishing 'signature' of the overall characteristic of the particle shape [8]. Durney and Meloy [5] have used statistical procedures to differentiate Fourier coefficients obtained from different populations. Fractal analysis [9, 10] has been also widely applied to particle shape characterization and is especially useful for highly complex shapes such as those of agglomerates. However, the approach adopted in the present work is based on an attempt to define shape in terms of physically recognizable features of the particles as can be seen from Figure 1 showing electron micrographs of –45μm size fractions for some of the cement samples examined. Table 3 for example lists main macroscopic shape descriptors used in the present analysis for shape characterization. It should be noted that the values of all these shape descriptors for spherical particles is unity except shape factor. For spherical particles shape factor is expected to be zero.



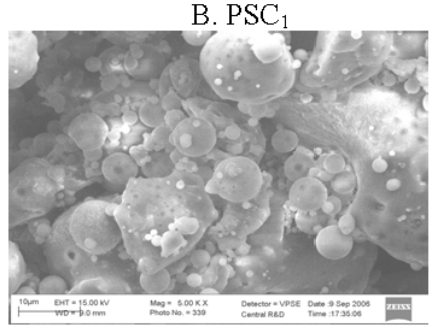
A. OPC_2



B. PSC_1



C. PPC_2



D. Fly Ash

Figure 1: SEM photomicrograph of –45µm size fraction of Cements and fly ash showing differences in morphological character of samples.

Table 3: Definitions of main macroscopical shape descriptors

Name	Formula	Comments
Form factor	$\frac{4\pi A}{P^2}$	Compares the surface area of the object (A) to that of a disk having same perimeter (P)
Aspect ratio	$\frac{L}{B}$	L is length of longest feret, B is breadth, length of shortest feret
Compactness	$\frac{\sqrt{4A/\pi}}{L}$	
Shape factor	$\left[\frac{P^2}{A} - 4\pi\right]$	
Fullness ratio	$\sqrt{\frac{A}{Convex \cdot A}}$	Convex A is the area of the polygon circumscribing the feature, formed by tangents to its boundary
Solidity	$\frac{A}{Convex \cdot A}$	
Convexity	$\sqrt{\frac{P}{Convex \cdot P}}$	Convex P is the length of the polygon circumscribing the feature, formed by tangents to its boundary

Figure 2 shows particle size distribution of the samples used in the study and Table 4 shows the physical properties of the cements used in the present work.

3.2 Analysis of shape descriptors for different size classes:

Figure 3 shows examples of form factor distributions of various size classes for two of the cements examined. In both the plots the distributions are shown as cumulative number distributions. Each of the size class in all the cements is observed to be having different form factor distribution. However, it is observed that except PPC there is no systematic variation in the form factor for the given size classes in case of remaining samples.

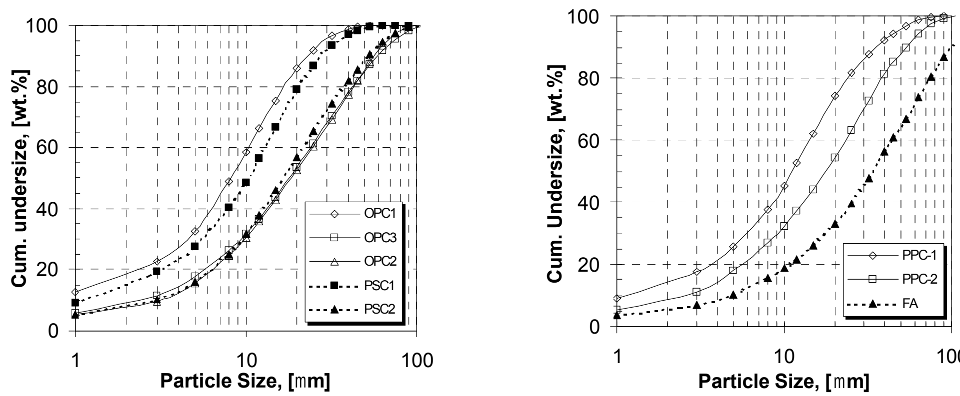


Figure 2: Particle size distributions of cement samples

Table 4: Physical properties of cement samples.

	OPC_1	OPC_2	OPC_3	PSC_1	PSC_2	PPC_1	PPC_2
Blaine [m^2/kg]	460	260	288	399	330	353	336
Sp. Gravity [-]	3.09	3.18	3.20	2.95	2.95	2.92	2.86
N.C [%]	29.0	26.0	26.0	30.5	29.5	30.0	29.3
Setting time [min]							
Initial	90	145	135	295	240	165	160
Final	150	185	170	345	285	215	205
Compressive Strength [MPa]							
1-D	29.9	22.3	22.8	9.6	12.5	14.8	15.3
3-D	43.4	36.3	38.6	24.7	27.8	26.2	27.5
7-D	49.6	49.6	49.4	42.7	44.7	40.1	42.3
28-D	58.2	67.7	64.1	61.8	65.1	61.1	63.1
Flow [mm]	99.1	98.1	132.1	70.8	86.1	96.3	113.3

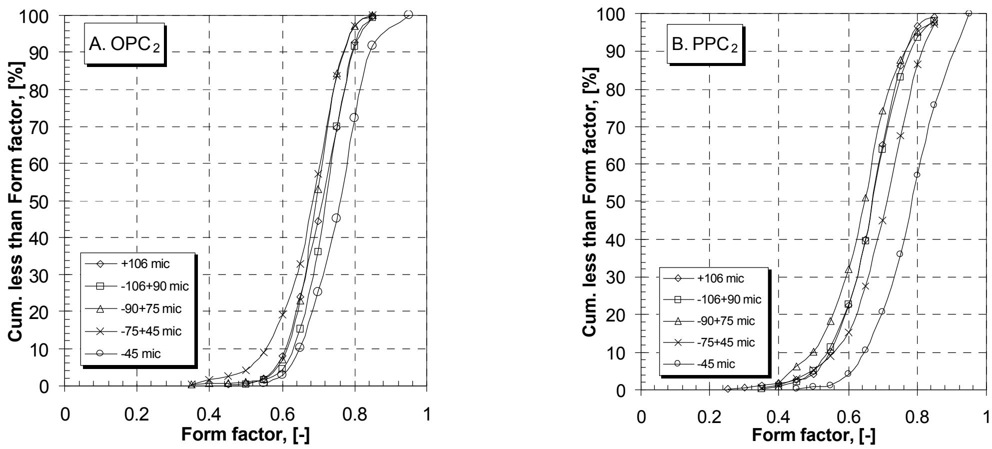


Figure 3: Form factor distributions of various size classes

In case of PPC it is observed that finer fractions of the cement tend to be more roundish approaching spherical geometry. This is probably due to the effect of fly ash particles, which are known to contain considerable amount of spherical particles. Moreover it is observed during microscopic analysis (both optical as well as SEM) that spheres below around 25-30μm do not get ground in the ball mills effectively leaving the spherical particles intact. Further it should also be noted that in the given grinding systems the fly ash is generally added after the ball mill and thus particles, which meet the size specification of the product are automatically separated in the high efficiency classifier thereby escaping any change in size modification. Therefore, presence of these ungrounded micro spheres can be expected to get reflected in improved form factor distribution in case of PPC.

Figure 4 shows examples of the aspect ratio distributions for two of cements in all the size classes. It was seen from the results that for coarser size fractions the distributions tend to be slightly narrower compared to –45μm fraction. Moreover for given aspect ratio –45μm particles are observed to be lower in quantities indicating more non-uniform particles in the finer sizes. It should be noted that as aspect ratio approaches unity the particles tend to be more roundish without much sharp projections/corners. Thus in all the cases coarser particles appear to be more spherical probably due to their effective morphological evolution involving mechanisms like chipping and abrasion of edges & corners.

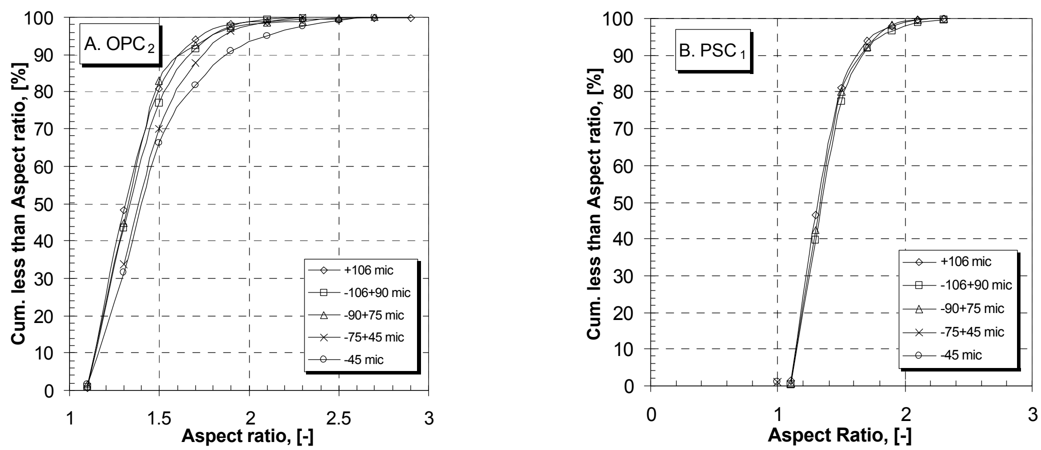


Figure 4: Aspect Ratio distributions of various cement size classes

This seems specifically to be the case with the Vertical Roller Mill samples since residence times of the product particles in these types of mills is quite higher as evident from their higher Blaine values as compared to other systems. But in spite of this, finer fractions do not get abraded enough due to classification action involved for resulting in lower aspect ratios. In case of PPC samples nearly 3-6% of the –45µm particles were observed to be near unity aspect ratio indicating presence of spherical particles introduced in the product through fly ash.

Figure 5 shows the shape factor distributions of two samples in different milling systems. It can be seen that the shape factor distribution becomes narrower with decreasing particle sizes. Moreover finer fractions tend to be more towards lower shape factors. In both the PPC samples particles having shape factor less than 2 are present in –45µm fraction in appreciable amounts. This is again an indication of fine well formed fly ash particles having near spherical geometry, which have escaped comminution action due to classification because of their meeting the desirable product size specifications.

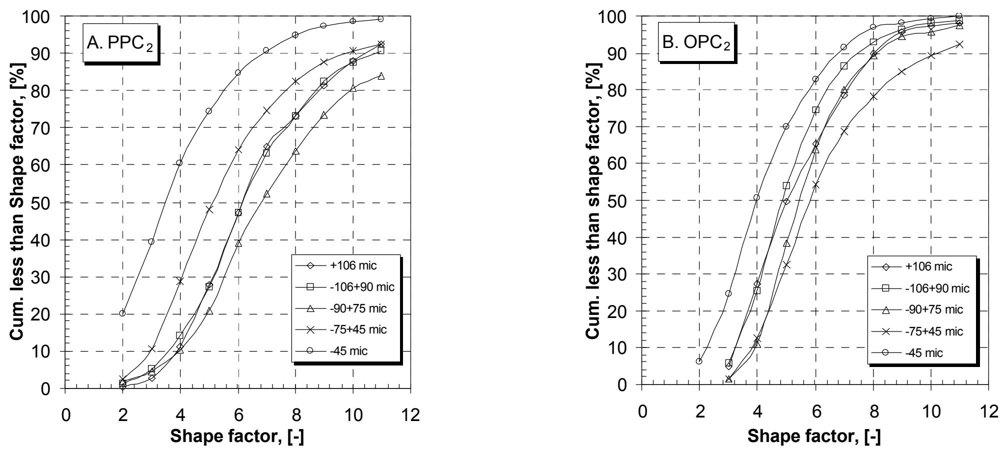


Figure 5: Shape factor distributions of two cement size classes

In all the other cement types although variations are observed in shape factor distributions amongst various size classes, a systematic trend is absent. Most of the cement fractions were found to be varying in the shape factor range of 2 to 8 except the OPC_2 sample (made in Roll Press). In case of this sample the particles are observed to be concentrated in the shape factor range of 4-10.

This behaviour can probably be attributed to the mechanism of massive fracture applied in the Roll Press. This leads to daughter particles having highly irregular shape. It was also observed in case of –45μm fraction of OPC_2 (made from Roll Press) that C_2S grains in clinker which are generally spherical in geometry get liberated from C_3S crystals at the boundaries of the clinker matrix due to high pressure employed in the process. Typical photograph of the said phenomena is shown in Figure 1(A) captured using SEM. The spherical particles shown in Figure 1(A) are analyzed chemically to be C_2S using EDAX facilities available with SEM. It can also be observed that typical grain sizes of C_2S ranges between 10-25 μm. Further, probably due to this phenomena shape distribution in case of –45μm in OPC_2 is observed to be quite separated than rest of the size fractions distributions shifting more towards lower shape factors. In case of OPC and PSC samples the shape distributions are also observed to be considerably steeper than that in case of PPC.

Figure 6 shows compactness, fullness ratio, solidity & convexity for five size classes of all the cement samples. The results related to these parameters indicated that the particles are concentrated in a very narrow range and presenting the results in terms of cumulative plots may not be very informative and convenient. Hence they are presented in the comparative form as shown in Figure 6. From the plot of compactness (Fig.6A) it can be seen that for all the cement samples except PPC the compactness decreases marginally with decreasing size indicating increased irregularity of particulate geometry. In case of PPC the presence of spherical particles in –45μm size class is probably leading slightly incremental compactness. To illustrate the point further, compactness of fly ash particles in the five size classes is also plotted in the Figure. It is clear that the compactness of the fly ash particles increases with decreasing particle size due to presence of highly regular particles. Further, in case of OPC_1 the compactness of all the size classes (except +45 & -45 μm) is observed to be greater than the other cements probably due to the shearing action applied between grinding rolls and table in the VRM thereby removing sharp edges and corners. Similar phenomena can also be observed for PSC_1 and PSC_2, which apply two different mechanisms for slag grinding. Consequently for PSC_2 particles massive fracture leads to irregular particles resulting in lower compactness than those in case of VRM.

However as far as fullness ratio (Fig. 6B) is concerned all the cement samples more or less vary in a very narrow band. For the reasons mentioned earlier previously fly ash particles show comparatively higher fullness ratio than the other samples.

Solidity of the particles as shown in Figure 6C in case of OPC_1 is again found to be quite higher than the other OPC products due to different stressing mechanisms applied in the process. Similarly as far as PSC is concerned, VRM product is observed to be having higher solidity than that in case of Roll Press. However this distinction of stressing mechanism seems to be less effective in case of –45μm size class particles probably due to classifier effect in case of VRM and non-escape of these fines during high compression fracture in compacted bed in case of Roll Press.

Finally as far as Convexity of the samples is concerned (as shown in Figure 6D) –45μm size class of all the products (including fly ash) is observed to be almost similar at the value of around 0.93 which is considerably higher than other size fractions. In case of PPC and fly ash this was expected due to presence of spherical particles in the populations. Again in case of Convexity VRM is found to be more favourable due to its shearing mechanism. Ball mill on the other hand is observed to be able to give lowest convexity particles amongst grinding systems considered as opposed to Roll press, which is found to be producing particle convexities intermediate to that of VRM and Ball Mill.

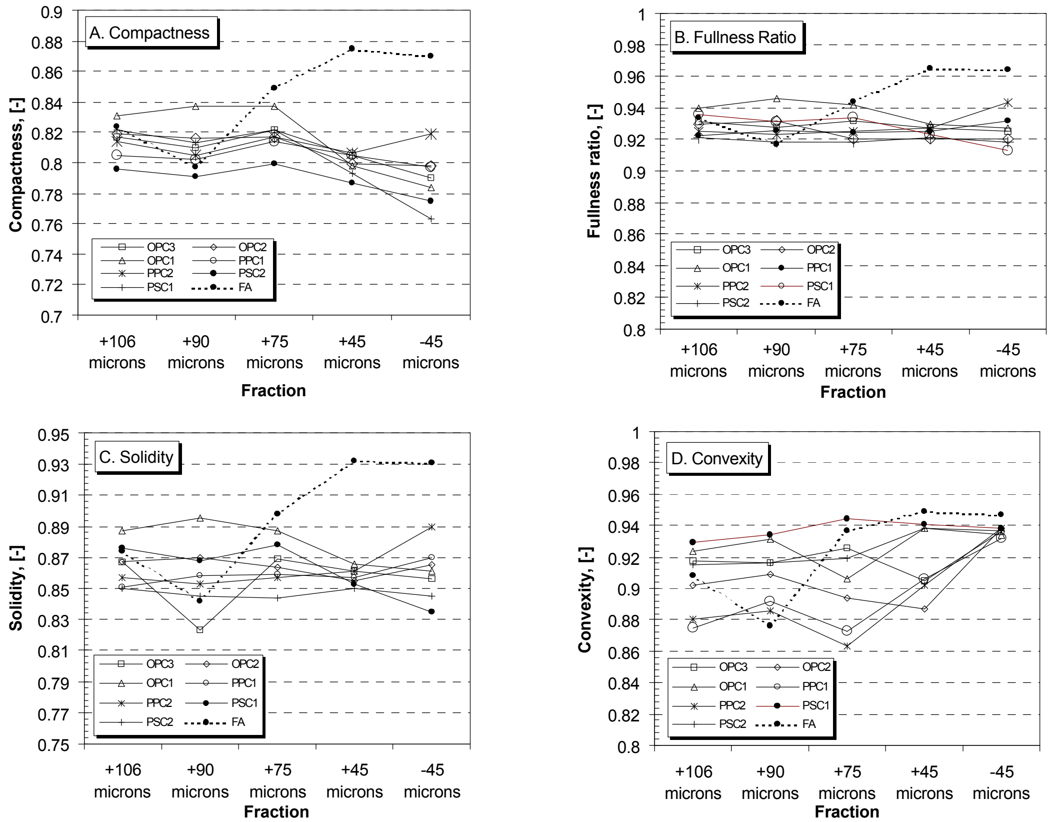


Figure 6: Shape descriptors namely Compactness, Fullness Ratio, Solidity and Convexity of the cement samples

3.3 Effect of milling system on product shape characteristics:

Figure 7-9 shows the effect of milling systems on the entire product shape characteristics of all the cements considered in the studies. In case of OPC cements aspect ratio (as shown in Figure 7A) the milling system is found out to be having negligible effect on the overall product aspect ratio. In case of PPC Ball mill is observed to be producing marginally higher aspect ratios for the product than that in combination of Roll Press and Ball mill as indicated in Figure 7B. This may be due to the cracks generated in the particles in the Roll Press, which are exploited for further size reduction in the Ball mill. This plot also shows the aspect ratio distribution of fly ash particles for reference. Due to their remarkably regular shapes fly ash particles seem to be desirable as far as aspect ratio is concerned. In case of PSC samples the Roll Press Ball mill combination is observed to be producing considerably finer aspect ratio distribution especially at the aspect ratios of 1.5 and below.

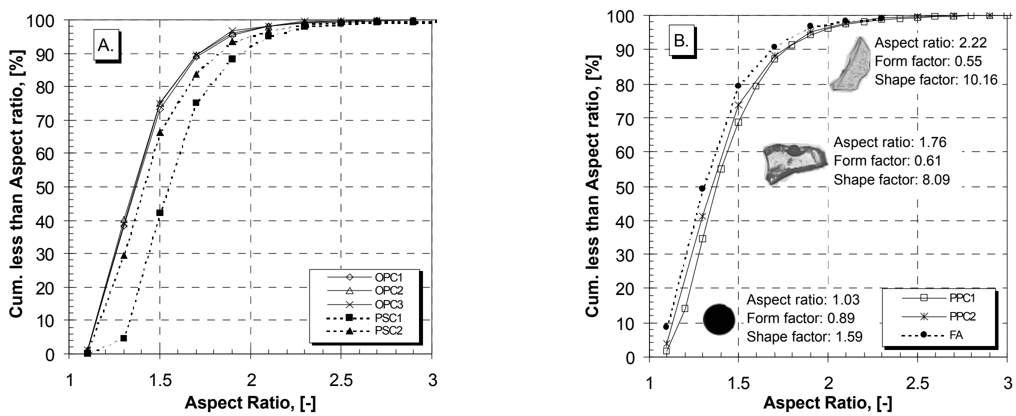


Figure 7: Effect of various milling systems on product aspect ratio of OPC, PPC and PSC samples.

Figure 8 shows the form factor for different cement samples produced using different comminution systems. In case of OPC cements VRM systems appears to be producing considerably roundish particles followed by Ball Mill and Roll Press. Obviously form factor is clearly seen to be governed by stressing mechanism of shearing in VRM and massive fracture in Roll Press. However the PPC sample is not observed to be much different in case of only Ball Mill and Roll Press & Ball Mill combination. It is suspected that the effect of Roll Press is being erased in the ball mills leading to almost similar form factors of the resulting products. On the other hand VRM is again observed to forming more roundish particles as compared to Roll Press in case of PSC as shown in Figure 8A.

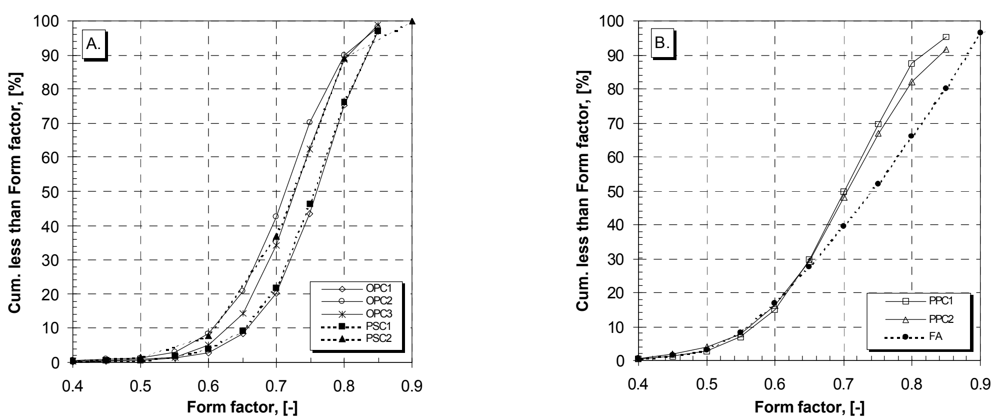


Figure 8: Effect of various milling systems on product Form factor of OPC, PPC and PSC samples.

Figure 9 shows effect of milling system on the shape factors of all the cement products considered in the work. Again in case of OPC VRM appear to be producing roundish particles followed by Ball Mill & lastly by the combination of Roll Press & Ball Mill. As stated earlier the effect of Ball mill is observed to be getting diluted in case of shape factors as well in case of PPC. Finally for PSC VRM system is confirmed to be producing considerably roundish particles than the Roll Press Ball Mill combination again pointing out effect of comminution mechanism on the particle morphology evolution.

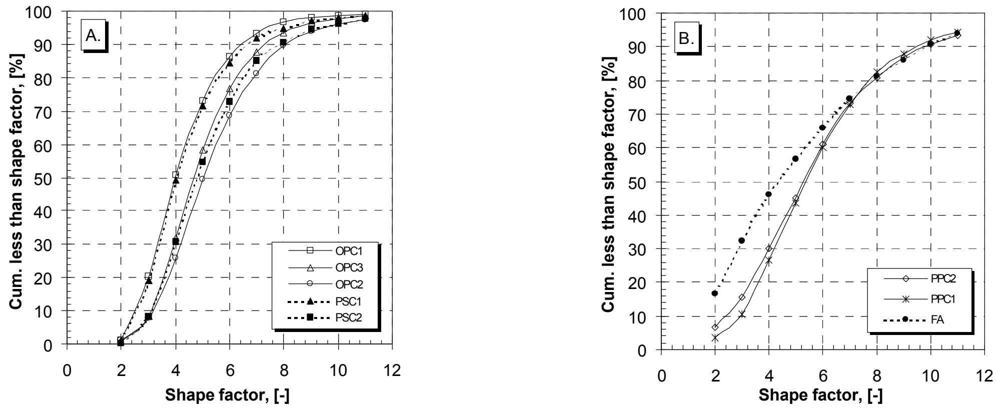


Figure 9: Effect of various milling systems on product shape factor of OPC, PPC and PSC samples.

3.4 Effect of shape descriptor of product on fresh cement properties:
Table 5 shows median (corresponding to 50% cumulative passing) and width of the shape descriptor distribution (ratio of 90% & 10% cumulative Passing) of the cements examined for Form factor, Aspect ratio and Shape factor along with the mini slump of the cements at water-cement ratio of 0.5.

Table 5: Shape descriptors of cement samples used in the work along with mini slump test results

	OPC_1	OPC_2	OPC_3	PSC_1	PSC_2	PPC_1	PPC_2
Form factor							
Median form factor	0.760	0.712	0.730	0.755	0.725	0.70	0.705
Width of form factor distribution	1.265	1.311	1.278	1.288	1.311	1.437	1.50
Aspect Ratio							
Median Aspect ratio	1.306	1.305	1.305	1.54	1.41	1.38	1.35
Width of Aspect Ratio distribution	1.480	1.480	1.480	1.477	1.578	1.467	1.558
Shape Factor							
Median shape factor	4.0	5.0	4.7	4.0	4.8	5.4	5.3
Width of shape factor distribution	2.48	2.50	2.14	2.68	2.52	3.13	4.08
Flow [mm]	99.1	98.1	132.1	86.1	70.8	96.3	113.3

It should be noted that for all the shape descriptors values approaching unity are desirable for having good flowability due to lower flow resistance offered in mini slump test. In absence of any linear correlation between the shape descriptors and flow an attempt was made to correlate median and width of the distribution of corresponding shape descriptor with flow using non-linear quadratic regression. Based on the results shape factor parameters were observed to be having a strong correlation with flow having co-efficient of correlation (R^2) more than 0.96. However the other two shape descriptors namely form factor and aspect ratio were found to be moderate correlations with R^2 of around 0.73. As an example a contour plot of shape factor distribution parameters with flow is shown in Figure 10. Thus it can be seen that morphology of the particles is having considerable role in deciding functional properties of cements.

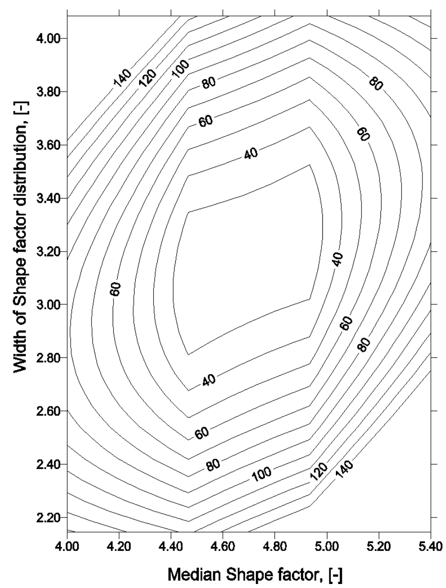


Figure 10: Relationship between shape factor distribution parameters and the flow properties of cements

Thus based on the shape descriptor results it is reasonable to assume that particle shape does play an important role in fresh cement properties. On the other hand properties like strength, setting times, etc are more governed by hydration reaction of the cement particles and hence by the corresponding surface area and therefore particle shape is not expected to alter these physical characteristics much.

4.0 Conclusions:

In the present work an attempt is made to characterize various cements from different milling systems in terms of their morphological characteristics by evaluating various physically realizable shape descriptors. The shape descriptors are evaluated for five size classes for each product and are observed to quite independent on the particle size. However the effect of milling system and consequently stressing mechanism on the morphological evolution of particles is observed to be rather distinguishable. Further, a correlation between shape descriptors & flow property is attempted using non-linear regression technique. Thus, these shape descriptors for the cements are observed to be playing an important role in fresh cement properties. Therefore concept of shape descriptor can be used effectively for understanding the role of milling systems on the cement particle morphology & corresponding functional properties.

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References:
[1] J.I. Bhatty, F.M. Miller and S.H. Kosmatka eds., Innovations in Portland Cement Manufacturing, Portland Cement Association, Skokie, (2004).
[2] C. Frances, N. Le Bolay, K. Belaroui and M.N. Pons, Particle morphology of ground gibbsite in different grinding environments, Int. J. Miner. Process, 61, (2001) pp. 41–56
[3] F. C. Bond, “Control Particle Shape and Size,” Chemical Engineering, (Aug. 1954) pp. 195-198
[4] C. B. Holt, “The Shape of Particles Produced by Comminution, A Review,” Powder Technol., 28. (1981) pp. 59-63.
[5] T. E. Durney and T. P. Meloy, “Particle Shape Effects due to Crushing Method and Size,” Intl. J. Miner. Process, 16. pp. 109-123 (1986).
[6] E. Kaya, R. Hogg, and S. R. Kumar, “Particle Shape Modification in Comminution”, KONA, No.20, (2002) pp. 188-195
[7] T. F. Dumm, and R. Hogg, “Characterization of Particle Shape,” Proc. of Int. Symp. on Respirable Dust in the Mineral Industries, SME, Littleton, CO, (1990) pp. 283-288.
[8] J. K. Beddow, and T. P. Meloy, Advanced Particulate Morphology, CRC Press, Boca Raton FL (1977).
[9] B. H. Kaye, “The description of Two-Dimensional Rugged boundaries in Fine particle Science by Means of Fractal Dimensions’,” Powder Technol., 46. (1986) pp. 245-254.
[10] J.C. Russ, The Image Processing Handbook, CRC Press, Boca Raton, FL, (1995).