Rheological Investigation of 50% Fly Ash Slurry at different Particle Size Range with and without Cetylpyridinium chloride

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Abstract

In thermal power plants pumping power required to transport fly ash slurry is directly proportional to the apparent viscosity of slurry. Smooth flow behaviour and drag properties of fly ash slurry depend on particle size of fly ash. Fly ash is a mixture of wide range of particle sizes. Study indicates that slurries composed of small particle sizes bear less viscosity even at higher shear rates and obeys power law based dilatant flow behaviour. In this work the effect of particle size on flow behaviour and drag properties of 50% (by weight) fly ash slurry is studied through experimentation. Flow behaviour of slurries are analysed with 'Oswald de Waele' rheological model which is a power law model. A study on the effect of 0.5% of CPC on the flow behaviour and viscosity values of these slurries is done.

1. Introduction

The use of coal as fuel in thermal power plants produces a large amount of fly ash and bottom ash. The production of fly ash is much more than bottom ash. Studies indicate [1] that in the year 2004-05 112 million tonnes of fly ash was produced and in 2011-12 it is expected to be 170 million tonnes. Hydraulic transportation of fly ash water slurry requires large amount of water. Fly ash slurry is a complex fluid (non-Newtonian fluid) composed of a fixed percentage of fly ash (by weight or by volume) and water. Generally, a lean mixture (about 20 to 25% of fly ash mixed with water) is used for transportation to save pumping power in thermal power plant, because at higher concentrations viscosity of slurry increases dramatically with shear rate and flow behaviour is non-newtonian in nature which in turn requires large pumping power. The advantages of using low concentrations of fly ash is that the apparent viscosity of slurry remains almost same at low as well as high shear rates and is almost predictable without the use of any complicated rheological model. Studies indicate [6] that at higher concentrations (40% fly ash) flow behaviour of slurry is dilatant (shear thickening) in nature. The size of particles plays an important role in determining the smooth flow behaviour of slurry. Small particles in a solution bear more stability; all the theories of entropic forces which create repulsion or attraction between particles are very well satisfied for small particle size solution [9, 14]. Also the stability effect created by additives which results in reduction of viscosity is strong on small particles due to their less mass and more surface area available.

We can see that problem with high concentration slurries is the increased viscosity induced at high shear rates and abrupt flow behaviour. However, it can be solved to some extent by using appropriate drag reducing additive; the effect of additive can be increased by using low particle size slurry. With this approach, drag properties of high concentration slurries can be reduced to appreciable extent making them suitable for pumping process. In this work, experiments were conducted on a rheometer with 50% fly ash (by weight 'Cw') slurries made from different size range particles. The effect of 0.5% by weight of Cetylpyridinium chloride (CPC) on drag properties of different particle size slurries is studied. Studies indicate [13] that rheological models are excellent tools to study the flow behaviour of high concentration fly ash slurries. A power law based rheological model named 'Oswald de Waele' model is used to calculate the apparent viscosity values of different slurries with and without additive and determine the nature of flow (dilatant, Newtonian or pseudoplastic).

2. Experimental details (materials and methods)

2.1 Fly ash used

Fly ash sample was collected from Guru Nanak Dev thermal power plant situated in Bhatinda (Punjab). EDS analysis of fly ash sample indicates that it is lignite in nature with low calcium content similar to class F of ASTM C618 [1] standard. The structure of fly ash is spherical as shown in SEM photographs below.

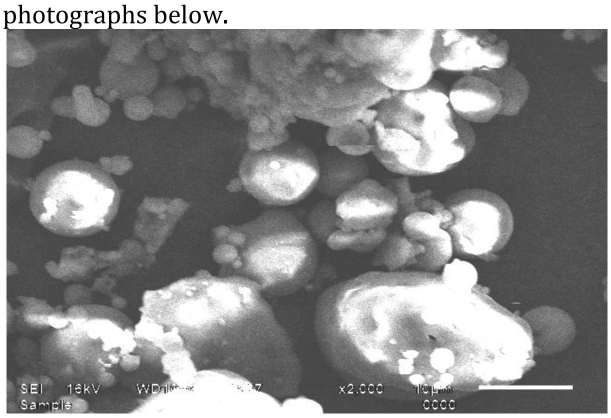

Fig. 1: Fly ash sample at 2000 magnification

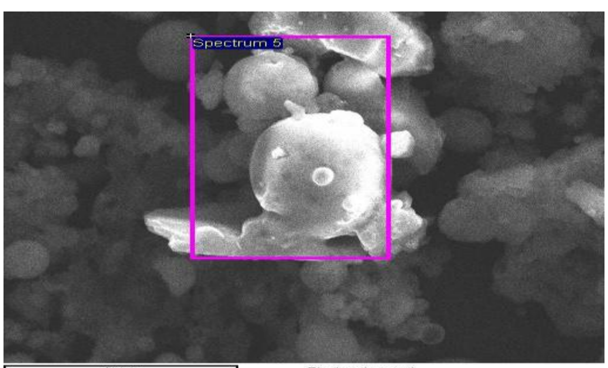

Fig. 2: Section of sample selected for EDS analysis

Tab. 1: EDS analysis of fly ash sample

Chemical composition of fly ash sample				
Element	Weight %	Atomic %	Compd%	Formula
C	6.74	10.69	24.69	CO2
Al	15.96	11.27	30.15	Al2O3
Si	17.09	11.60	36.57	SiO2
K	0.90	0.44	1.09	K2O
Ca	0.35	0.17	0.49	CaO
Ti	1.39	0.55	2.32	TiO2
Fe	1.27	0.43	1.64	FeO
Cu	1.36	0.41	1.70	CuO
Zn	1.10	0.32	1.37	ZnO
O	53.84	64.13	-	-

2.2 Additive used

Cetylpyridinium chloride is a cationic quaternary ammonium compound [4] with molecular formula $C_{21}H_{33}ClN.H_2O$. It is a solid pale yellow at room temperature. It is used in some types of mouthwashes, toothpastes [12] and throat sprays. It is an antiseptic that kills bacterial and other microorganisms. It is also used as an ingredient in certain pesticides.

Tab. 2: Physical and chemical properties of CPC

S No.	Parameters	Value
1	CAS number	15.96
2	Molecular Weight (M.W.)	11.27
3	Minimum Assay activity	30.15
4	Melting point	Al2O3
5	pH (1% aqueous solution)	4.7-5.7
6	Sulphated ash	Max. 0.2%
7	Water content	4.5-5.5%
8	Heavy metals	Max. 0.002%
9	Pyridine, Acidity	Passes test

CPC has a long chain of hydrocarbon which is hydrophobic in nature; it has a bulky benzyl group as a head. Studies indicate [11] that CPC molecules form worm shaped micelles in a water solution after crossing their critical micelle concentration (cmc) value.

2.3 Preparation of slurry at 50% concentration and specific particle size range

Particles of different size ranges were obtained through dry mechanical sieving process. Fly ash sample was dried in an oven at 200^0C temperature for 60minutes. Dried sample was sieved through meshes of different mesh sizes specified in microns using a horizontal type mechanical sieving machine. After sieving the sample of particles collected in each sieve were packed in air tight plastic envelops to prevent any moisture gain. All the samples were prepared by weight. Total of 8 samples were prepared with and without CPC. 50% concentration slurry was prepared for each particle size range sample, by mixing the weighted amount of particles with water using magnetic stirrer for 20 minutes. Following table shows a detailed composition of slurry in each case

Tab. 3: Slurry composition in grams and % concentration by weight

S no.	Particle Size range (µm)	Fly ash (gm) 50% Cw	CPC (gm) 0.5% Cw	Water (ml) 50% Cw
1	150 to 106	40	0	40
2	106 to 75	40	0	40
3	75 to 53	40	0	40
4	53 to 0	40	0	40
5	150 to 106	40	0.4	40
6	106 to 75	40	0.4	40
7	75 to 53	40	0.4	40
8	53 to 0	40	0.4	40

2.3 Specifications of rheometer

Flow behaviour was studied on a rheometer (Make: Anton Paar, Model: Rheolab QC). It has concentric cylinder measuring system according to ISO 3219 and DIN 53019 [8]. Shear rates can be varied from 10^{-2} to 4000 s^{-1}. During experimentation values of viscosity and shear stress were calculated at 20 different shear rates ranging from $0s^{-1}$ to $500s^{-1}$. The temperature was kept constant throughout the measurements. Specifications of the geometry used during experimentation are given below. The geometry used is specifically designed for the viscosity measurements of high concentration slurries.

Tab. 4: Dimensions of geometry used in rheometer

Cup dia. Rc (mm)	Rotor dia. Re (mm)	Rc /Re	Measuring gap
14.46	15.96	1.08	1.13

2.4 Oswald de Waele rheological model

It is a version of basic power law model [13, 6]; this model is used for slurries which have viscosity relations that are function of shear rate, but not a function of time of application of shear [13]. It is simple and less time consuming model. Studies indicate that this model is not much accurate at very low shear rates, but accurately approximates the apparent viscosity values at high shear rates. The equations representing this model are:

$\tau = K \gamma n$ and $\eta = K \gamma (n-1)$

Taking log on both sides

$\ln(\tau) = \ln(K) + n*\ln(\gamma)$ (model on log-log plot)

Here, K = consistency coefficient [pa/s], n= viscosity index, τ = shear stress [pa], γ = shear rate [1/s], η = apparent viscosity [mpa-s].

With this model the value of n determines the flow behaviour of slurry as follows.

- n<1 (Shear thinning fluid or pseudoplastic fluid)
- n=1 (Newtonian fluid)
- n>1 (Shear thickening fluid or dilatant fluid)

In this model, K is the value of viscosity at γ =1, in general higher value of K shows more viscous behaviour.

3. Results and Discussions

3.1 Particle size distribution (PSD) of fly ash

PSD of fly ash was estimated using the process of dry mechanical sieving as explained before. The distribution is almost normal in nature as shown in figure 3. We can see that fly ash consists of wide range of particle sizes. About 40% of fly ash lie in the range of 53 to 75µm size, 24% lie less than 53µm size and 23% lie in 75 to 106µm range. From cumulative retained graph, we can see that these 3 particle size ranges cover about 87% of the total weight of fly ash. It will be seen in the upcoming results that the overall viscosity of fly ash slurry depends mainly on these 3 particle size ranges.

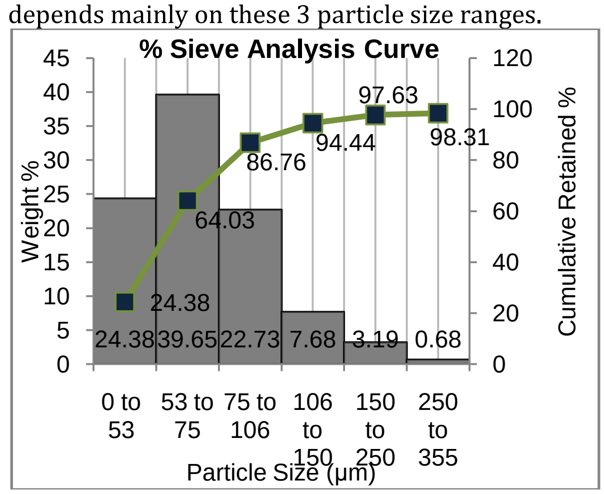

Fig. 3: Particle size distribution of fly ash with curve for cumulative weight retained.

3.2 Effect of particle size on viscosity of 50% fly ash slurry with and without CPC

Figure 4 to 7 compare the viscosity values of slurries made with different particle sizes, we can see that small particles bear less viscosity, also slurries with particles less than 100µm size obeys power law. Apparent viscosity values of slurries made from more than 100µm particle size are unpredictable and cannot be modelled using Oswald de Waele model. With large particle size initial viscosity goes very high as shown in figure 4. Flow behaviour is improved with addition of CPC in particle size range less than 100µm. In the size range of 150 to 106µm, addition of CPC has increased the viscosity; we can say that in high particle size solution like this, the repulsive forces created by CPC's hydrophobic tail are not enough as compared to inertial and gravitational forces created by the large particles, all the CPC molecules remain in water solution and form rapid micelles which aggregate under shear flow as shown in figure 4.

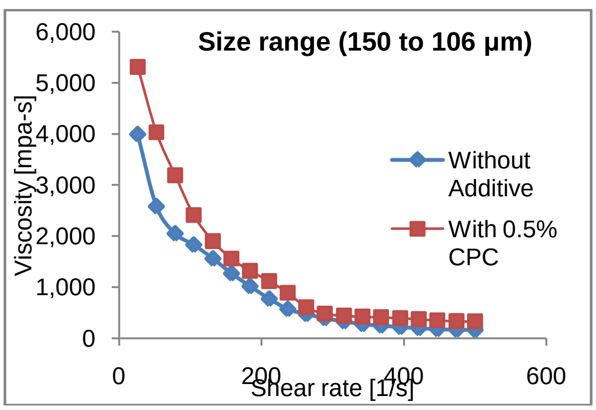

Fig. 4: 50% fly ash slurry with particle size range of 150 to 106µm

From figure 5 to 7, we see that with addition of 0.5% of CPC apparent viscosity values of slurries with particle size less than 100µm have reduced to an appreciable extent.

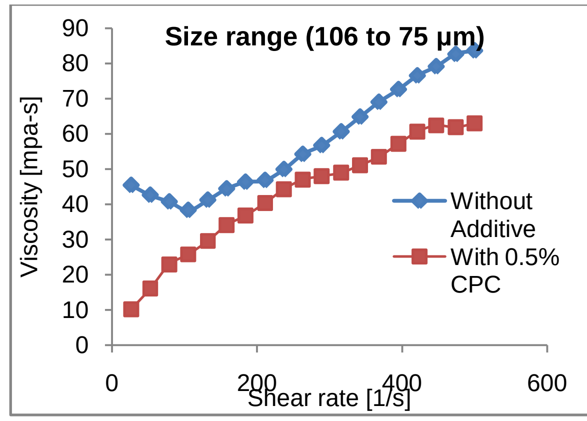

Fig. 5: 50% fly ash slurry with particle size range of 106 to 75µm

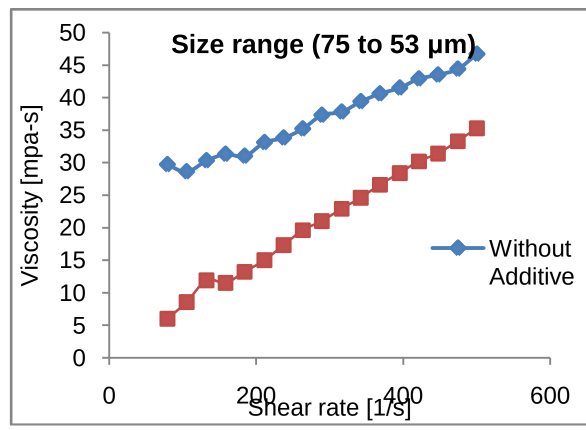

Fig. 6: 50% fly ash slurry with particle size range of 75 to 53µm

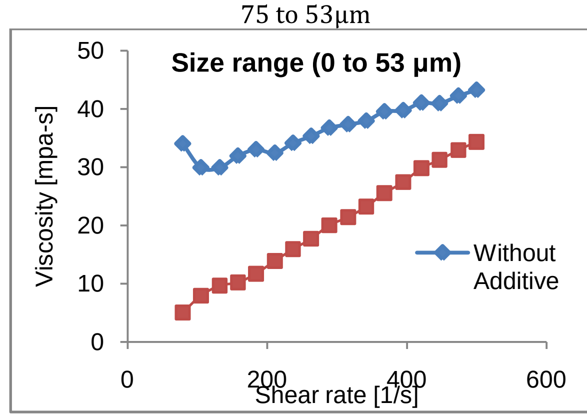

Fig. 7: 50% fly ash slurry with particle size range of 53 to 0µm

Table 5 and 6 below compare the flow properties of slurry obtained through Oswald model without and with CPC.

Tab. 5: Flow parameters of slurry without CPC

Particle size range (µm)	106 to 75	75 to 53	53 to 0

Viscosity index 'n'	1.53535	1.27341	1.25152
Coeff. of regression 'r'	0.99747	0.99791	0.99925
ln(K)	-5.8447	-4.8275	-4.7281
Consistency coeff. 'K'	0.0029	0.00801	0.00884

Tab. 6: Flow parameters of slurry with 0.5% C_w CPC

Particle size range (μm)	106 to 75	75 to 53	53 to 0
Viscosity index 'n'	1.61462	1.9255091	2.01141
Coeff. of regression 'r'	0.99957	0.9989767	0.99918
ln(K)	-6.528	-9.1038	-9.6551
Consistency coeff. 'K'	0.00146	0.0001112	$6.4x10^{-5}$

From table 5, the flow is dilatant in nature, since viscosity index 'n' is greater than 1 in each case. We can see from table 5 that even at 50% concentration slurry is approaching Newtonian flow behaviour as the particle size is reduced, since in the size range of 53 to 0 μm viscosity index is very close to 1. From table 6 we can see that with addition of CPC, dilatant behaviour is increased but consistency coefficient 'K' has reduced dramatically. Reduction in consistency coefficient 'K' clearly indicates a dramatic decrease in viscosity of slurries. Coefficient of regression 'r' in both the tables is greater than 0.99 which indicates the reliability of regression of shear stress vs shear rate lines plotted on logarithmic scale to calculate the apparent viscosity values using rheological model [3].

3.3 Modelling results for slurries with and without CPC

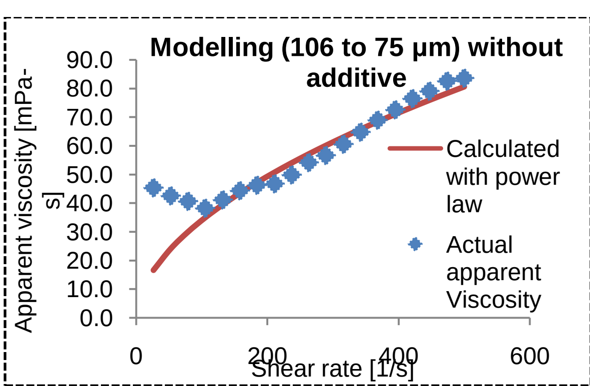

Fig. 8: Modelled apparent viscosity values for slurry without CPC

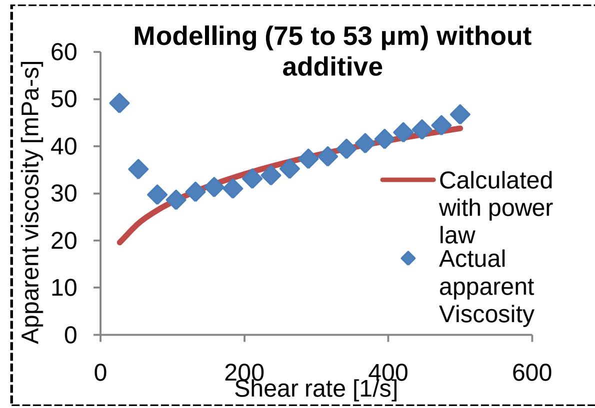

Fig. 9: Modelled apparent viscosity values for slurry without CPC

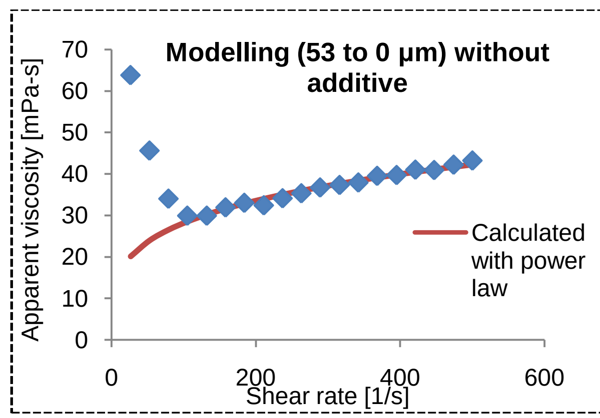

Fig. 10: Modelled apparent viscosity values for slurry without CPC

From figures 8, 9 and 10 we can see that modelled values are in good approximation with the actual apparent viscosity values. Figure 10 shows that with small particle size, flow behaviour of slurry accurately follows the power law model. In general, every mathematical model has 'x_{min}' value below which it gives unpredictable results. We can see that the results predicted by this model are not satisfactory below $100s^{-1}$ shear rate. The starting viscosity values (from 0 to $100s^{-1}$) in all the 3 cases are much greater than the predicted value. Figures 11, 12 and 13 display's the modelled apparent viscosity values in case of slurries containing 0.5% of CPC. With addition of CPC 'x_{min}' value of the model has reduced from $100s^{-1}$ to as low as $20s^{-1}$. Clearly flow behaviour is improved as modelled values are lying very closely to actual viscosity values. From figure 12 and 13 we can see that viscosity values form almost a straight line, which indicates that shear stress increase is perfectly obeying the power law and driving with very smooth flow behaviour even at low shear rates.

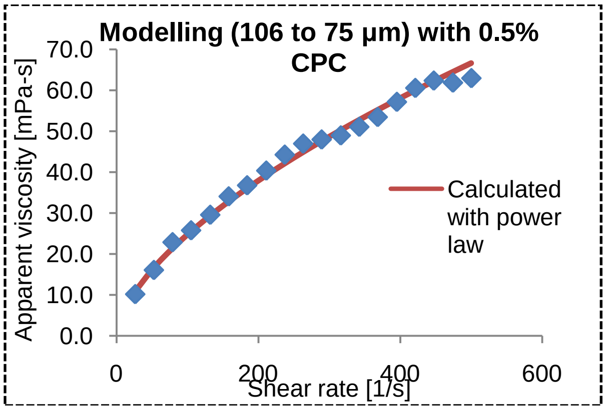

Fig. 11: Modelled apparent viscosity values for slurry containing 0.5% of CPC

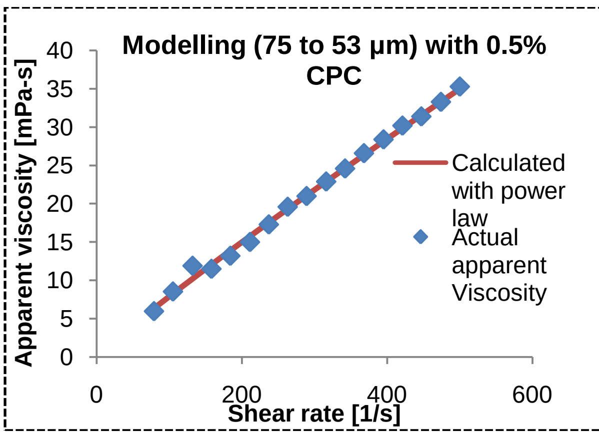

Fig. 12: Modelled apparent viscosity values for slurry containing 0.5% of CPC

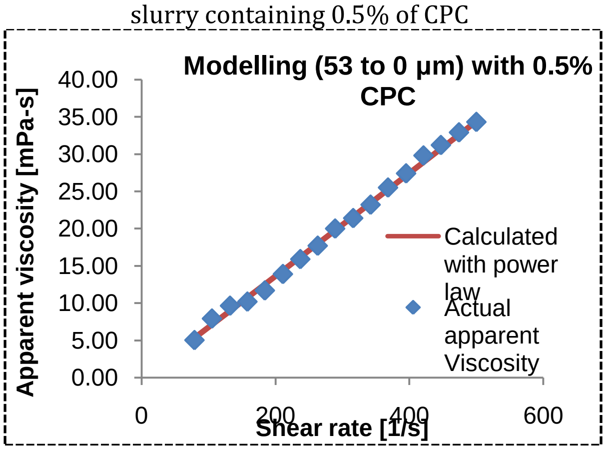

Fig. 13: Modelled apparent viscosity values for slurry containing 0.5% of CPC

4. Conclusion

Clearly, small particle size slurry bear smooth flow behaviour and less viscosity. Sieve analysis shows 87% of fly ash lies in the size range of about 0 to 100μm size. Flow behaviour of slurries made from these particles is dilatant in nature and obeys power law. 0.5% of CPC has greatly reduced the apparent viscosity values of these slurries. Modelling results showed that the problem of large apparent viscosities at low shear rates was eliminated by the use of CPC. The results indicate that CPC molecules help increase the hydrophobic nature of surface of fly ash particles [13], thereby increasing the hydrophobic repulsion and establishing stability in the solution even at 50% concentration of fly ash. The effectiveness of CPC in drag reduction directly depends on particle size of fly ash.

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