

Effect of Cetylpyridinium chloride, Triton x-100 and Sodium Dodecyl Sulfate on rheology of fly ash slurry

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Abstract- Low values of viscosity and shear stress of fly ash slurry demands less pumping power in thermal power plants. In this work rheological behavior of fly ash slurry is studied. Study indicates that, additives of different nature (cationic, anionic and non-ionic polymer) help reduce viscosity and shear stress of slurry. Effect of 3 concentrations of additives (0.5%, 1% and 1.5% by weight) on viscosity of 40% fly ash slurry was studied. Viscosity index 'n' in each case was calculated using Oswald de Waele rheological model. Comparison is done between 3 additives in terms of effect on drag properties of slurry. Effect on pH of slurry with and without additives was studied.

Index Terms- Additives, drag reduction, fly ash, rheology, modeling

I. INTRODUCTION

It is a well known fact that small percentage of drag reducing additives (cationic, non-ionic and anionic in nature) can help reduce viscosity [9,10], surface tension and other properties when added to water. Disposal of residual fly ash is one of the major problems faced by thermal power plants today [6]; the work presented here is an attempt to solve this problem to some extent. To transport this fly ash the method involved is hydraulic transmission, in which a lean mixture of fly ash and water is transported through pipelines to ash ponds, currently 20 to 25% of fly ash by weight (C_w) is mixed with water to form slurry for transportation in power plants. Although it's a clean method but it requires a large percentage of water, it would be wiser to use more percentage of fly ash in slurry. Drag reducing additives [9, 2] can help reduce the values of viscosity and shear stresses of slurry, thus improving flow behavior and creating a good chance to increase the percentage of fly ash in slurry. It can save valuable water to some extent. Comparing the actual apparent viscosity values of slurry with the values calculated using a mathematical rheological model gives the idea of good flow behavior [4]. There are many rheological models available. The applicability of model to particular slurry depends on flow behavior of slurry. In this work 'Oswald de Waele' rheological model is used to calculate apparent viscosity values of slurry with and without additives and results are compared with actual data. Viscosity index (a parameter which indicates whether flow is dilatant, Newtonian or pseudoplastic) 'n' is calculated using this model. Three different drag reducing additives different in respect to the charge on the surface were studied, they are Cetylpyridinium Chloride [11] (referred to as CPC), Triton x-100 (referred to as triton) and Sodium Dodecyl sulfate [12] (referred to as SDS). CPC is cationic quaternary ammonium compound

[11] and solid pale yellow at room temperature. It is used in some types of mouthwashes, toothpastes [15], throat sprays etc. It is an antiseptic that kills bacteria and other microorganisms. It is also used as an ingredient in certain pesticides. Triton x-100 is a non-ionic surfactant very viscous at room temperature, it has a hydrophilic polyethylene oxide group (on average it has 9.5 ethylene oxide units) and a hydrocarbon hydrophilic group. SDS is an organic anionic surfactant derived from coconut and palm oils, it is used in many cleaning products [12], and it is an organosulfate consisting of a 12-carbon tail attached to a sulfate group, giving it the amphiphilic properties required of a detergent.

Recent studies have indicated that cationic surfactant mostly create an effective drag reduction when used in combination with organic salts [5, 2, 1, 9]. Here, effect of these additives is studied individually without the presence of organic salt. Optimal concentration of additive required is estimated by analyzing the experimental data. Comparison is made between these 3 additives in terms of their effectiveness in drag reduction of slurry and effect on overall pH of slurry.

II. EXPERIMENTAL DETAILS (MATERIALS AND METHODS)

A. Fly ash used

Lignite fly ash similar to class F of ASTM C618 [6] standard was collected directly from Guru Nanak Dev thermal plant situated in Bhatinda (Punjab). The structure of fly ash particle is shown below through SEM microphotograph at 5000 magnification.

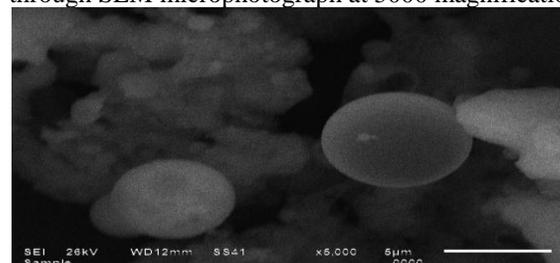


Fig. 1: Fly ash at 1000 magnification

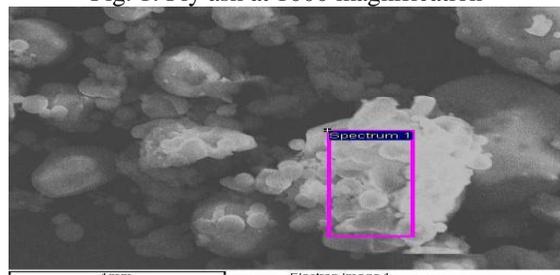


Fig. 2: Section of sample selected for EDS

Tab. I: EDS analysis of fly ash sample

Chemical composition of fly ash sample				
Element	Weight %	Atomic %	Compound %	Formula
C	6.74	10.69	24.69	CO ₂
Al	15.96	11.27	30.15	Al ₂ O ₃
Si	17.09	11.60	36.57	SiO ₂
K	0.90	0.44	1.09	K ₂ O
Ca	0.35	0.17	0.49	CaO
Ti	1.39	0.55	2.32	TiO ₂
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	-	-

B. Additives used

Cetylpyridinium chloride (Molecular formula: C₂₁H₃₈N.H₂O, Molar mass: 358.01 g mol⁻¹, melting point: 80 to 84°C), Triton x-100 (Molecular formula: C₁₄H₂₂O (C₂H₄O)₉, 99% pure, density: 1.07g/cm³, boiling point > 2000°C), Sodium Dodecyl Sulfate (Molecular formula: C₁₂H₂₅OSO₃Na, Molar mass: 288.38 g mol⁻¹, density: 1.01 g/cm³, melting point 206°C).

C. Preparation of fly ash water slurry at fixed concentration mixed with additives

Fly ash concentration was kept constant at 40% by weight and additives were added at different dosages of 0.5%, 1% and 1.5% of the total solution, to prepare this mixture, 40ml of water was taken in 100cm³ beaker and 26.666 grams of fly ash was weighted on a weighing scale. Additives were weighted based on the percentage required and added to mixture of fly ash and water, the resulting mixture was mixed thoroughly on a magnetic stirrer, and kept for 10 minutes for the release of entrapped air, and again shaken with hand before use. The solution was then poured into the cylinder of rheometer and finally attached to the concentric attachment on rheometer to take readings, the following table II shows concentration involved in different samples prepared.

Tab. II: Slurry composition in grams and % by weight

Sample no.	Fly ash (gm)	Additive (gm)	Water (ml)
1	26.666 (40% C _w)	0.33 (0.5% C _w)	40 (60% C _w)
2	26.666 (40% C _w)	0.66 (1% C _w)	40 (60% C _w)
3	26.666 (40% C _w)	0.99 (1.5% C _w)	40 (60% C _w)

D. Rheometer Specifications

Rheological properties were calculated on a rheometer (Make: Anton Paar, Model: Rheolab QC). It has concentric cylinder measuring systems according to ISO 3219 and DIN 53019. Shear rate can be varied from 10⁻² to 4000 1/s. 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.

Tab. III: Dimensions of geometry used in rheometer

Rheolab QC	Cup dia. Rc (mm)	Rotor dia. Re (mm)	Rc/Re	Measuring gap
SN80717904; FW 1.24	14.461	13.332	1.084	1.129

E. Rheological Model used

In general, a model is used for non-newtonian fluids which have viscosity relations that are function of shear rate, but not a function of time of application of shear[4]. There are many rheological models available, the model used here to study the flow behaviour of slurry is Oswald de Waele rheological model[4,13]. It is a version of general power law model[13], and its applicability can be estimated by observing the log-log plot of dependent and independent variables which must be approximately a straight line, this model is frequently used in rheological modelling because of its simplicity and wider applicability[2]. The equations representing this model is:

$$\tau = K \gamma^n \quad \text{and} \quad \eta = K \gamma^{(n-1)}$$

taking log on both sides
 $\ln(\tau) = \ln(K) + n \cdot \ln(\gamma)$ (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].

According to 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 $\gamma=1$, in general higher value of K shows more visous behaviour.

III. RESULTS AND DISCUSSIONS

A. Effect of CPC on flow behavior of 40% fly ash slurry

Figure 3 compare the viscosity values of slurry with and without CPC. Appreciable amount of reduction in viscosity is obtained in the shear range of 0 to 260s⁻¹. Also in this range the effect produced by the 3 different dosages of additives is almost the same. At higher shear rates (260s⁻¹ to 500s⁻¹) there is a change in the pattern of viscosity curve, and we can see an increase in viscosity in this range. This increase in viscosity at higher shear rates is associated with aggregation of micelles induced by the high shear rate flow [9]

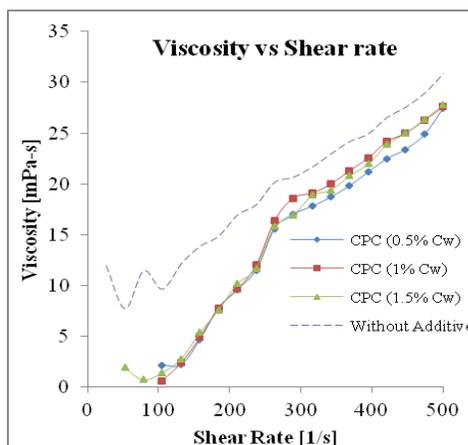


Fig. 3: Change in viscosity with addition of CPC

Tab. IV: Change in viscosity index and consistency coefficient with CPC

Modeling data calculated using 'Oswald de Waele' model			
0% CPC	0.5% CPC	1% CPC	1.5% CPC
n=1.606187	n=2.165245	n=2.201008	n= 2.337201
ln(K)=-7.30	ln(K)=-10.81	ln(K)=-10.96	ln(K)=-11.78
K=0.000672	K=2.01x10 ⁻⁵	K=1.72x10 ⁻⁵	K=7.58x10 ⁻⁶

It can be seen that the process of micelle aggregation started at 230s⁻¹, which created a bend and disrupted the straight line smooth pattern of viscosity increase. We can at higher shear rates; slurry with 0.5% CPC has less viscosity than slurries with 1% and 1.5% CPC, because higher concentrations of additives resulted in generation of more micelles [4, 9] which aggregate under higher shear flow. We can see from table IV that dilatant behavior is increasing with increase in concentration of CPC. From figure 5 we can see the flow behavior of slurry with CPC still obeys power law and actual viscosity values can be approximated using modeled values.

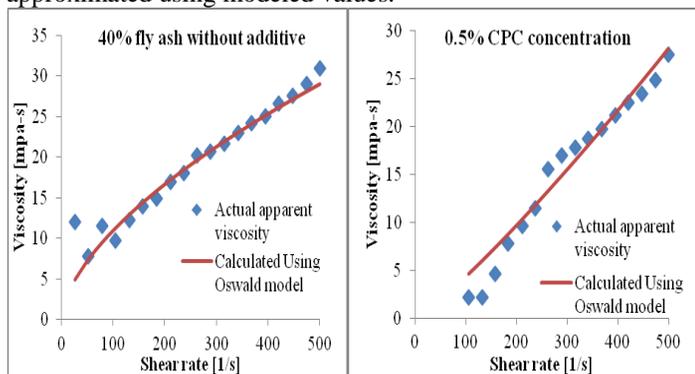


Fig. 4: 40% fly ash slurry

Fig. 5: slurry with 0.5% CPC

B. Effect of SDS on flow behavior of 40% fly ash slurry

SDS is anionic in nature with long hydrophobic tail. From figure 6, viscosity of slurry decreases with increase in the dosage of SDS. The phenomenon of aggregation of micelles at higher shear rates (more than 269s⁻¹) is observed. Results obtained from 1.5% of SDS are better as compared to 0.5% and 1% of SDS. The use of high dosage of SDS is also economical, as it is derived from inexpensive coconut and palm oil and hence has its

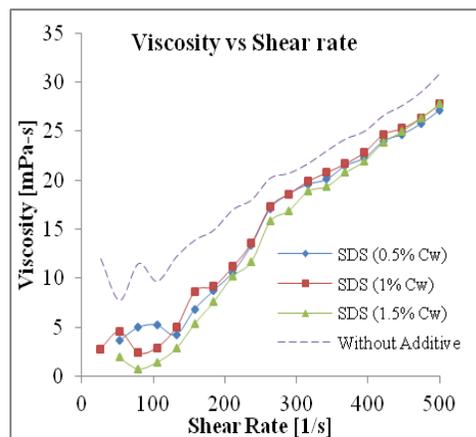


Fig. 6: Change in viscosity with addition of SDS

cheap manufacturing cost. The anionic head of SDS acts on the surface of fly ash particle, the hydrophobic tail creates hydrophobic repulsion between these particles preventing sedimentation and aggregation.

Tab. V: Change in viscosity index and consistency coefficient with SDS

Modeling data calculated using 'Oswald de Waele' model			
0% SDS	0.5% SDS	1% SDS	1.5% SDS
n=1.606187	n=2.029817	n=1.968560	n= 2.357599
ln(K)=-7.30	ln(K)=-9.97	ln(K)=-9.63	ln(K)=-11.92
K=0.000672	K=4.64x10 ⁻⁵	K=6.65x10 ⁻⁵	K=6.62x10 ⁻⁶

With SDS viscosity index of slurry increased, overall dilatant behavior is maintained around n=2 with appreciable decrease in viscosity and shear stress even at low dosage of SDS.

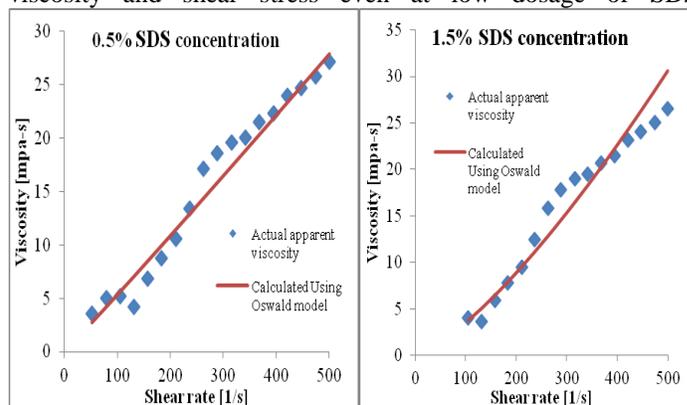


Fig. 7: Slurry with 0.5% SDS

Fig. 8: slurry with 1.5% SDS

We can see from figure 7 and 8 that as the dosage of SDS is increased, although viscosity is decreased, but flow behaviour is not as smooth as it was at low concentrations of SDS.

C. Effect of Triton x-100 on flow behaviour of 40% fly ash slurry

Studies indicate that polymer additives like Triton help in reduction of wall friction[17]. Polymer additives when dissolved in solvent, the polymer chains adopt various forms of shapes such as random coil, an extended configuration or a helix[16]. The polymeric chains can expand leading to significant increase in viscosity of solution. At high shear rates (300s⁻¹ to 500s⁻¹) stretching of polymer chain increases effective viscosity in the

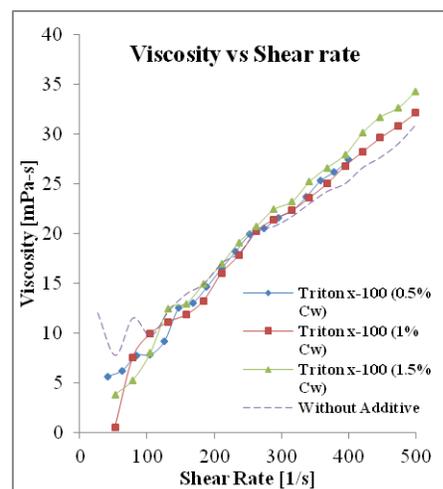


Fig. 9: Change in viscosity with addition of Triton x-100

buffer layer of turbulent flow by increasing elongational viscosity[18]. This increase in viscosity at buffer layer results in reduction of wall friction[17]. Although viscosity is increased, but flow behaviour is improved with addition of triton x-100.

Tab. VI: Change in viscosity index and consistency coefficient with Triton x-100

Modeling data calculated using 'Oswald de Waele' model			
0% Triton	0.5% Triton	1% Triton	1.5% Triton
n=1.606187	n=1.785695	n=1.798672	n= 1.965052
ln(K)= -7.30	ln(K)= -8.32	ln(K)= -8.40	ln(K)= -9.30
K=0.000672	K=0.000243	K=0.000225	K=9.09x10 ⁻⁵

Figure 10 and 11 shows the smooth flow behaviour of slurry obtained at higher concentrations of Triton x-100. With slurries containing triton the model is giving accurate values of apparent viscosities even at low shear rates such as 50s⁻¹ as shown below.

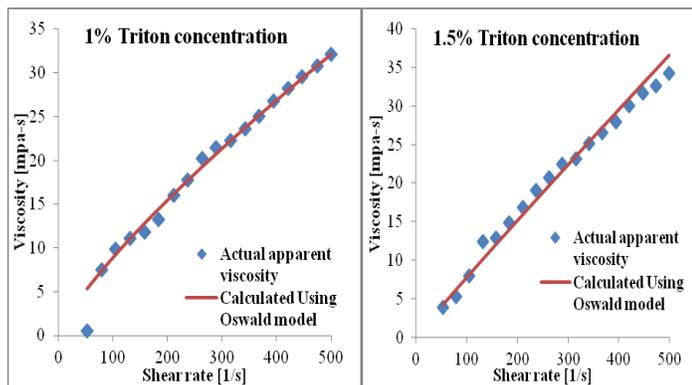


Fig. 10: slurry at 1% triton

Fig. 11: slurry at 1.5% triton

D. Effect of CPC, SDS and Triton x-100 on pH of fly ash slurry

pH of slurry affects the fertility of soil, acidic slurries can make the soil infertile. pH analysis of slurries containing different dosages of additives indicate that, in all the 3 cases pH is alkaline. There is very little increase in pH with addition of 1.5% CPC as shown in figure 12. We can see that increase in pH of slurry with addition of 1.5% SDS is much more than that of CPC. Triton x-100 lies in the middle as shown below.

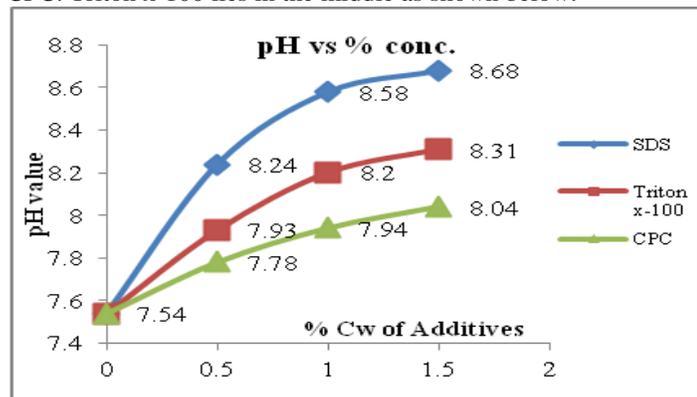


Fig. 12: Change in pH of 40% fly ash slurry with addition of CPC, SDS and Triton x-100

IV. CONCLUSION

Clearly additives play a crucial role in reducing drag properties of fly ash slurry. In spite of their nature (cationic or anionic), CPC and SDS help reduce viscosity of slurry. Non-ionic polymer additives like Triton x-100 help improve flow behavior and

reduce wall friction. At lower shear rates (25s⁻¹ to 300s⁻¹) CPC and SDS help reduce viscosity and shear stress to an appreciable extent. Power law model such as Oswald de Waele rheological model is an excellent tool to study the smooth flow behaviors of fly ash slurries; the model is applicable even after addition of additives and gives approximately the values of apparent viscosity at any shear rate. 0.5% of CPC is the optimal concentration both at low and high shear rates. Slurry mixed with 1.5% of SDS showed better results than slurries containing 0.5% or 1% of SDS. Overall dilatant behavior has increased after addition of additives. pH results showed that in the case of all the 3 additives slurry is alkaline and not acidic in nature, acidic slurries are known to effect fertility of soil and slow down the microbial activity in soil. It can be seen that the property of ionic additives to form charged complexes [2] with fly ash particles help improve the smooth flow behavior of slurry and reduce the effect of drag properties.

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