Rheological Characteristics of Fly Ash Slurry at Varying Temperature Environment with and without an Additive

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Abstract

Transportation of fly ash is a major problem in its efficient disposal. The main problem associated with fly ash transportation is that the particles settle down sooner than desired. The primary objective of this investigation is that not only the fly ash particles should remain floated till it reaches the end but also settle down after that. As a part of the research program, the slurry concentration was kept at 30% (by weight). Rheological tests were conducted using Advanced Computerized Rheometer. Fly ash slurry was prepared using ordinary tap water. Zeta potential was measured to test the stability of the colloidal fly ash particles using Malvern Zeta Sizer instrument. Surface tension was also measured to know the drag reduction behavior of the fly ash slurry by using Surface Tensiometer. The rheological behavior of the fly ash slurry was determined at varying temperature environment with and without an additive. Cetyltrimethyl Ammonium Bromide (CTAB) concentration of 0.1%, 0.2%, 0.3%, 0.4%, and 0.5% (by weight) was used as an additive with equal amount of a counter-ion (Sodium Salicylate). The test results and flow diagrams are generated using Rheoplus software and are presented in this paper. Suitable discussions and conclusions are made based on the research findings.

KEYWORDS: fly ash, slurry, rheology, shear stress, shear rate, viscosity

1.0 INTRODUCTION

About 50% of the fly ash generated in India is send to the ash ponds. As the demand for electrical energy is going up and up, more number of coal based thermal power plants are bound to come up. During 2006-07 generation of fly ash in India were around 130 million tones out of which only about 60 million tones was used gainfully and the rest 70 million tone was sent to ash ponds.[1,2] One of the major difficulties in disposal fly ash is its quick settlement in the hydraulic pipelines during its transportation. It is desirable that fly ash particles should remain water borne for a reasonable period of time before settling. In this study the role of a cationic surfactant was evaluated to achieve this objective.

Slurry pipelines are used to transport solid particulate materials using water or any other liquid as a carrier fluid. These pipelines are used either for long distance transport of bulk materials, like mineral ore to processing plants, coal to thermal power plants or for disposal of waste material like fly ash, mill tailings etc. to the disposal sites. Slurry pipelines today have also been accepted by various industries as an attractive mode of solid transportation because of its low maintenance cost, and being an eco-friendly system. In thermal power plants, these pipelines are used for disposal of fly ash/bed ash/bottom ash to ash pond area. These pipe lines currently carry lean slurry concentration with solid content of about 15% to 20% only.[3-7]

In slurry transportation the presence of solid particles leads to drastic change in the flow behavior, which affects the pressure drop considerably across the pipeline. Course particulate slurries require high operating velocities for transportation resulting in higher specific energy consumption per unit solid throughput.[3] Transportation of non-settling solids would result in lower energy consumption and better operational conditions.
The use of surface active agents (surfactants) as drag reducers in slurry transportation through pipe lines is investigated. These agents when added to a liquid, reduces its surface tension, thereby increasing its spreading and wetting properties. These aqueous solutions can even reduce up to 80% of the drag in a turbulent straight pipe flow in a wide range of temperature environment.[8] They are frequently used by various industries to disperse aqueous suspensions for their processes such as in corrosion inhibition, in ore floatation, to promote oil flow in porous rocks, and to produce aerosols. Many researchers have investigated the characteristics of such a dilute surfactant solution, but limited studies are reported about the use of these agents for the transportation of fly ash slurry in the pipe lines. Therefore, in the present investigation, an attempt has been made to evaluate the rheological behavior of the fly ash slurry with and without a surface-active agent.

The cationic surfactant, Cetyltrimethyl Ammonium Bromide (CTAB), $C_{19}H_{42}BrN$, was used in the present study to modify the surface properties of the fly ash particles. Since fly ash is being transported through ordinary water medium, tap water dissolved with CTAB was used for preparation of the fly ash slurry. Cationic surfactant (CTAB) was chosen because it is known to be less affected by calcium or sodium ions naturally found in tap water.[9] A counter-ion, Sodium Salicylate (NaSal), HOC_6H_4COONa, was also added to the slurry at the same weight concentration as that of the surface-active agent.[10, 11]

Keeping this in mind, fly ash samples obtained from Ennore Thermal Power Plant (Tamilnadu, India) was selected for determining the rheological behavior at varying temperature environment ranging from 20^0C to 40^0C with and without an additive. The effect of surfactant as an additive was studied at different concentrations varying from 0.1% to 0.5% (by weight). Based on the rheological data generated, suitable discussions and conclusions are presented in this paper.

2.0 Materials and methods

2.1 Fly ash

Fly ash sample was collected from the thermal power plant directly from the hoppers of Electrostatic Precipitator (ESP). Table-1 and Figure 1 shows the particle size distribution of the fly ash used for this investigation. The particle size distribution is known to have a strong influence on the hydrodynamics of surface modification and final modification effectiveness. In most cases, a fine size distribution is favored for effective cover of surfactant on the surface of particles in the wet modification process. The particle size distribution of raw fly ash was determined by Malvern Particle Size Analyzer (Model-Master Sizer 2000 ver. 5.22, U.K). The curve shown in Figure 1 is the shape of a normal distribution in mathematics. The majority of the fly ash particles are in the size range of 1µm to 50µm, with the average size being 9.042µm. The BET specific surface area of raw fly ash was 2.36m^2/gm. Table-2 presents the physical properties and the chemical composition of the fly ash sample investigated. The results of SEM microphotographs at 5000 and 1000 magnification inferred that the fly ash particles are round in shape which would help in the smooth flow of particles in the hydraulic pipelines due to ball bearing effect (Figure 2).

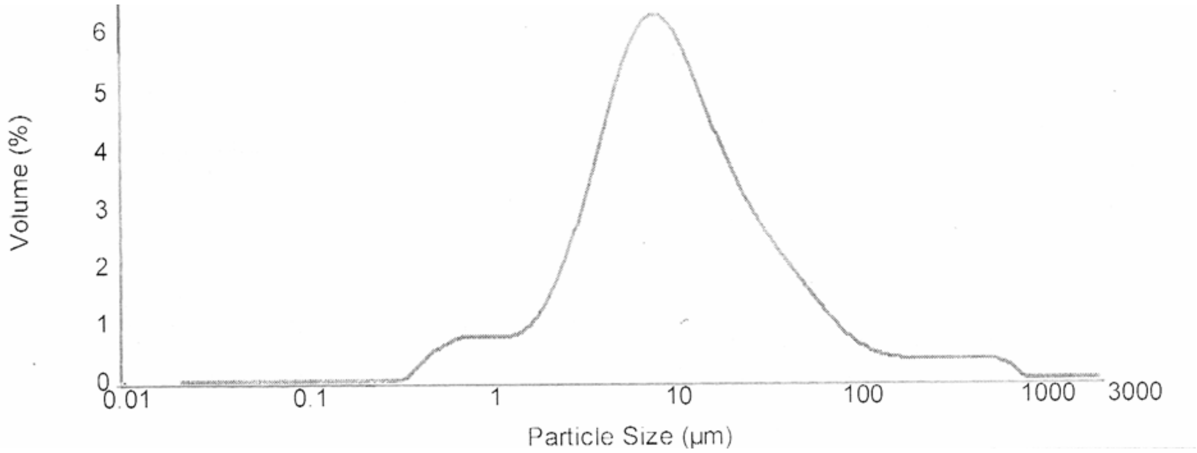

Figure 1: Particle size distribution of fly ash sample

Table-1: Results of particle size analysis of fly ash sample

Sample	Size range (%)			Uniformity Co-efficient, C_u
	< 1 µm	1 µm - 50 µm	> 50 µm	
Fly ash	3.66	87.80	08.54	2.32

Table-2: Physical and chemical properties of fly ash sample

Sample	Specific gravity	Specific surface area (m^2/gm)		Moisture content (%)		Wet density (g/cc)		Turbidity (NTU)
Fly Ash	2.20	2.36		0.200		1.75		459
	Chemical Composition, Elements (weight %)							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2	Na_2O	MgO
	56.77	31.83	2.82	0.78	1.96	2.77	0.68	2.39

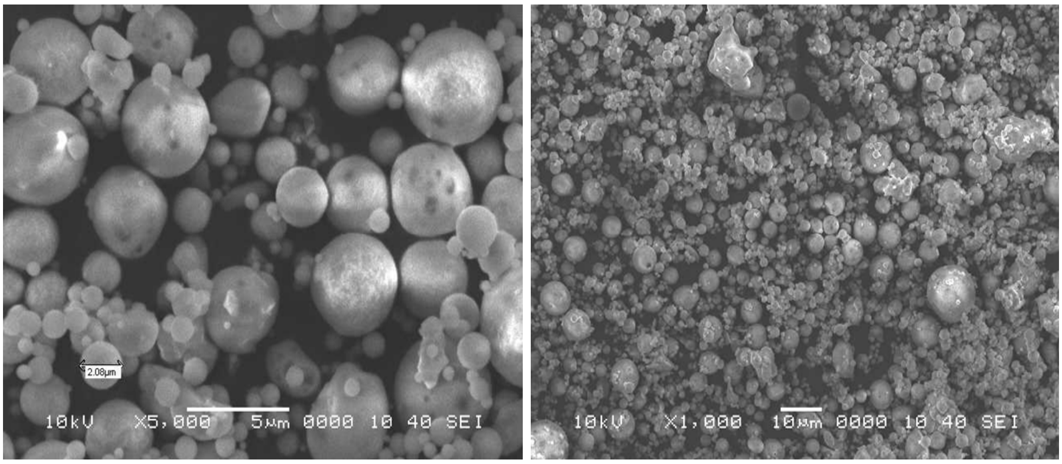

Figure 2: SEM Photomicrographs of untreated fly ash sample at 5000 and 1000 Magnification

2.2 Surfactant

The surfactant, used in the present study was having a molecular weight of 364.46. CTAB is a cationic surfactant and is known to be very effective for drag reduction when accompanied with suitable counter-ions. It is a non-reactive and non-toxic reagent. The various dosage of surfactant can affect the effectiveness of surface modification significantly. The hydrophobic group which is a long chain hydrocarbon with 19 carbons in the structure of the surfactant is attached to the fly ash particle, converting it from hydrophilic to hydrophobic property (Figure 3). Table-3 presents the physical and chemical properties of the surfactant used in this investigation.

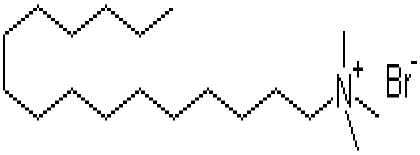

Figure 3: Molecular structure of the surfactant[12]

Table-3: Physical and chemical properties of the surfactant (CTAB)

Sl. No.	Parameters	Value in percentage
1	Minimum Assay value	99
2	Heavy metals (as Pb)	0.001
3	Iron (Fe)	0.001
4	Sulphated ash	0.1
5	Loss on drying	1.0

2.3 Counter-ion

The counter-ion used for this investigation was Sodium Salicylate (NaSal), Chemical formula- HOC_6H_4COONa was having a molecular weight of 160.10. It was used as it was supplied without any modification. Table-4 presents the physical and chemical properties of the counter-ion.

Table 4: Physical and chemical properties of the counter-ion (NaSal)

Sl. No.	Parameters	Value in %
1	Minimum assay (calculated to dried material)	99
Maximum limits of impurities		
2	Loss on drying at 105^0 C	0.5
3	Chloride (Cl)	0.02
4	Sulphate (SO_4)	0.05
5	Heavy metals (as Pb)	0.002

3.0 EXPERIMENTAL PROCEDURE AND RANGE OF PARAMETERS

3.1 Experimental Procedure

An advanced Computerized Rheometer (Model MCR101 manufactured by M/s Anton Paar Company Ltd., Germany) was used for obtaining the relation between the rate of shear and shear stress of fly ash slurry sample at varying temperature environment. The rheometer (Coaxial cylindrical measuring system, Standard: ISO 3219)[13] assembly consisting of a motor with attached gear box system for changing the speed in steps of equal ratio was used for this investigation. The cylindrical measuring bob (diameter: 26.664 mm and height: 40.014 mm) is attached to a torsion bar and the concentric measuring cup (diameter: 28.922 mm) can be rotated at the desired speed. Temperature was controlled by a fluid bath circulator to $\pm 0.5^0$C of the desired temperature. Shear viscosity was measured by a shear rate sweep experiment. The waiting time before taking the data was set at 20 seconds minimum at each shear rate. Viscosity at each shear rate was calculated as the average of five measurements.

3.2 Preparation of the sample

For rheometric tests, 100ml of the suspension was prepared by mixing 30 gram of fly ash with 70 ml of tap water to obtain the desired concentration (C_w). An electronic analytical balance with a resolution of 10^{-3} gm was used for weighing the materials accurately. The suspension was mixed gently by a glass rod, taking care to avoid attrition of the particles. The suspension after preparation was covered by aluminum foil to avoid evaporation of water from the suspension, and is allowed to wet for at least one hour before conducting the tests in a constant temperature bath (circulator). About 19 ml of the slurry sample was poured into the cup. The slurry was well stirred by a glass rod and the bob was lowered into the cup so that the free surface touches the top of the bob. The tests were conducted at shear rates varying from 25, 50, 100, 200, 300, 400, and 500 per second at a fixed temperature environment. These shear rates were selected because the recommended maximum shear stress was at a shear rate of about 511 sec^{-1}. Exposing cement slurry to shear rate above 511 sec^{-1} has been reported to generate inconsistent results.[14, 15] The temperature was varied from 20^0C to 40^0C and experiments were repeated at the above shear rates. The above temperature range was selected based on the average temperature variation during the various seasons of a year in India during which the fly ash slurry is to be transported. The tables and flow curves were generated from the measured data by the Rheoplus software.

3.3 Range of parameters

Experimental studies were carried out for six different solid liquid mixtures at varying temperature environment. The concentration of surfactants used was 0, 0.1, 0.2, 0.3, 0.4, and 0.5% (by weight) of the total slurry. This range of surfactant concentration was selected based on literature review.[3,16,17] About 30 grams of oven dried fly ash sample was stirred well and the surfactant was added and mixed thoroughly taking care of the attrition of the particles. An equal amount of counter-ion (same as surfactant concentration) was added to the slurry to take care of the ions present in the tap water. Fly ash slurry samples with varying surfactant dosage and counter-ion was prepared and their rheological characteristics were evaluated at varying temperature environment and shear rates as presented in Table-5.

Table-5: Sample ID, Parametric variations and suspension characteristic features

Sample No.	Fly ash (gm)	Surfactant (gm)	Counter-ion (gm)	Water (ml)	Solid Conc. C_w (by wt.)	Surface Tension (mN/m)	Zeta Potential (mV)	pH at 25^0C
1	29.0	0.5	0.5	70	30	32.178	+35.200	7.73
2	29.2	0.4	0.4	70	30	32.249	+34.534	7.63
3	29.4	0.3	0.3	70	30	31.830	+33.800	7.24
4	29.6	0.2	0.2	70	30	31.902	+32.100	7.64
5	29.8	0.1	0.1	70	30	33.305	+31.700	7.66
6	30.0	0.0	0.0	70	30	57.900	-25.000	7.30

An equal amount of counter-ion was added to the prepared sample to reduce ion radius of CTAB and to take care of the ions present in the tap water.[10, 11] The additive was added to the water at the time of preparation of the slurry. Thus six samples were prepared as depicted in Table-5 for rheological and flow behavior investigation. The rates of shear during the measurements were varied from 25 to 500s^{-1}. These ranges correspond to the magnitudes of shear rates usually expected in low concentration fly ash pipeline transportation systems. The lower shear rate range of 2 to 20 s^{-1} was used by Seshadri *et al.* 2005 for highly concentrated slurries i.e. $C_w \approx 68\%$ (by wt.).[3] They also used shear rates ranging from 20 to 120 per second for high concentration slurry of C_w (by weight) of 60 and 65 percent for their rheological investigation.[4,5] Because these ranges correspond to the magnitudes of shear rates usually expected in high concentration pipeline transportation systems as advocated by them.

4.0 RESULTS AND DISCUSSION

The results of the present investigation are presented and the corresponding rheograms and flow curves are depicted in Figures (4-15). The findings of the results are discussed with respect to varying temperature environment and surfactant concentration. The plots of experimental data in terms of shear stress (τ) and shear rate ($\dot{\gamma}$) in the range of 25 to 500 per second are presented in Figures (4-7). It is seen that the variation of the shear stress with shear rate at all slurry combinations with additives for fly ash sample at varying temperature environment almost follows a linear trend with a zero yield stress (τ_y) which is expected at low concentration slurry transportation systems conforming to the observations made by Seshadri *et al.* 2005.[3] The straight line behavior is almost Newtonian in nature. The straight line equation can be expressed in the form of:

$\tau = \eta\, \dot{\gamma}$...... [1]

Where τ = shear stress, η= viscosity and $\dot{\gamma}$ = shear rate. The straight line equation is fitted for each set of data. It is seen that the values of yield stress (τ_y) are almost zero for all the sets of data. This implies that the fly ash slurry for the data presented, shows a Newtonian behavior with some shear thinning effects and can be represented by Newtonian model outlined in the equation [1]. It is also seen that the viscosity and shear stress decreases for all the cases with increase in temperature as expected from the fundamental properties of viscous materials.

4.1 Effect of surfactants on fly ash slurry rheology

Figures (4-7) shows the rheograms of the fly ash slurries at different temperature environment and effect of surfactant dosage (0.2%, 0.3%, 0.4%, and 0.5% by weight) on the flow behavior at varying shear rates. It is observed from the results that the shear stress of the slurries decreased with increasing temperature at a fixed shear rate for all the surfactant dosage investigated. From the figures it is observed that the fly ash slurries showed shear thinning behavior at 20^0C and 25^0C which is a desirable feature for any hydraulic transport system. At 30^0C, 35^0C and 40^0C the slurries almost showed straight line (Newtonian) behavior with a zero yield stress. The untreated slurry showed uneven flow behavior which is not reported here.

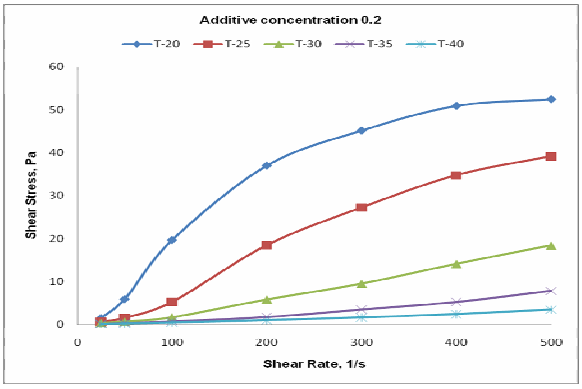

Figure 4. Rheogram of fly ash slurry with additive concentration 0.2%

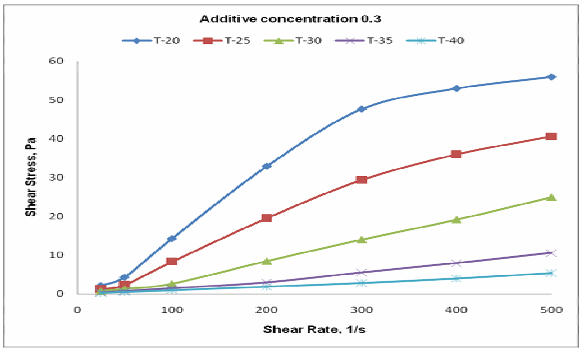

Figure 5. Rheogram of fly ash slurry with additive concentration 0.3%

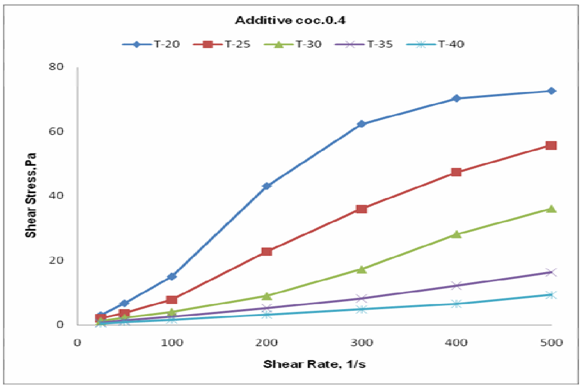

Figure 6. Rheogram of fly ash slurry with additive concentration 0.4%

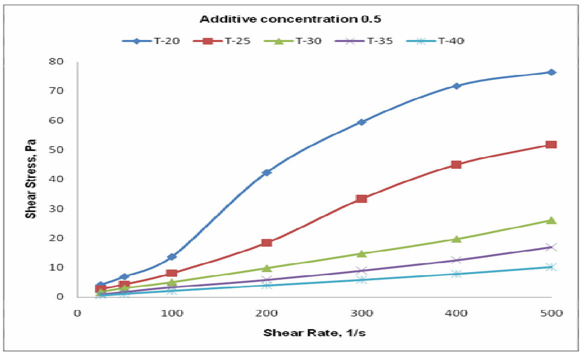

Figure 7. Rheogram of fly ash slurry with additive concentration 0.5%

4.2 Shear viscosity

Figures (8-11) shows the shear viscosity of fly ash slurries with an additive concentration of 0.2%, 0.3%, 0.4% and 0.5% at varying temperature environment. From these figures it is observed that the shear viscosity decreases sharply from 20^0C to 40^0C reaching a minimum value at 40^0C with the shear rates varying from 25 to 500 per second for all the additive ranges tested. It is also observed that shear thinning behavior is observed at 20^0C and 25^0C for all the slurries tested. At 30^0C, 35^0C and 40^0C the viscosities of the slurries almost remained unchanged for the shear rates varying from 25 to $500s^{-1}$. The untreated fly ash slurry showed erratic flow behavior which is not presented here.

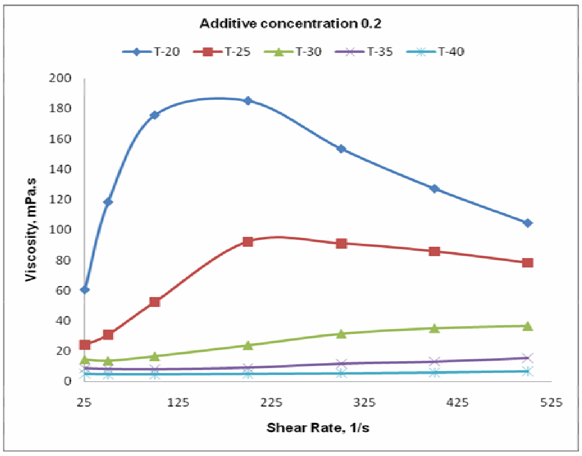

Figure 8. Flow curve of fly ash slurry with additive concentration 0.2%

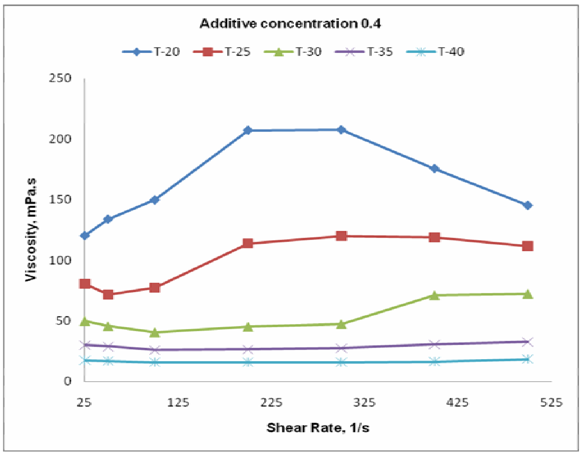

Figure 10. Flow curve of fly ash slurry with additive concentration 0.4%

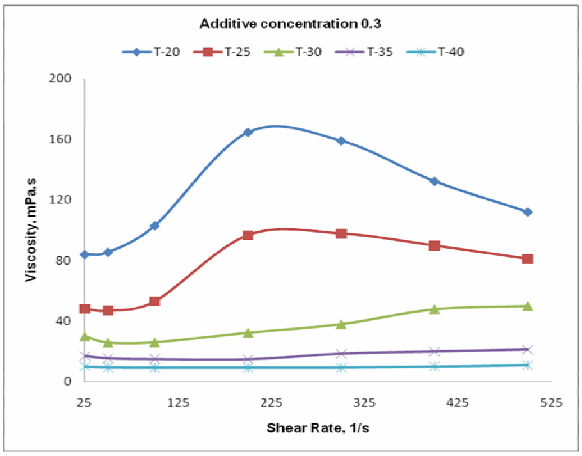

Figure 9. Flow curve of fly ash slurry with additive concentration 0.3%

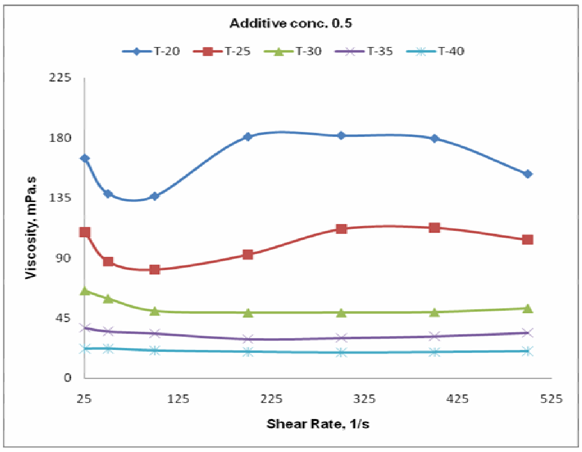

Figure 11. Flow curve of fly ash slurry with additive concentration 0.5

4.3 Effect of temperature on fly ash slurry rheology

Temperature affects the modification of the fly ash particles by decreasing the viscosities as the temperature increased. This could be due to the enhanced dissolving activity of the surfactant at higher temperatures. Based on the viscosity results in

Figures (12-15), the optimum modification temperatures for treated fly ash were found to be 30^{0}C to 40^{0}C. It was also observed from the results that in the range of tests carried out, the values of both shear stress and viscosity decreased with increase in temperature which is expected from the fundamental properties of any viscous material.[18,19] This can be attributed to the increase in the consistency of the slurries, which decreases the resistance to shear. Secondly, when relatively larger numbers of solid particles are present, a comparatively larger value of initial stress is required to start the process of shearing. Since the fly ash used in this investigation is very fine in nature so the yield stress is almost zero. This decrease can be explained on the basis of the fact that the number of particles and the surface area of the solids per unit volume of the slurry decreases with reduction in solid concentration. The Viscosity vs. temperature plots for fly ash slurry at different shear rates are exhibited in Figures (12-15). From these figures it is observed that the decrease in viscosity with increasing temperature is spectacular from 20^{0}C to 30^{0}C and after that the viscosity decrease was marginal till it reaches to 40^{0}C for all the shear rates tested. This may be due to the formation of spherical micelles which are said to exist only in relatively dilute solutions.[20-22] The untreated fly ash slurry did not show any definite trend, hence not reported here.

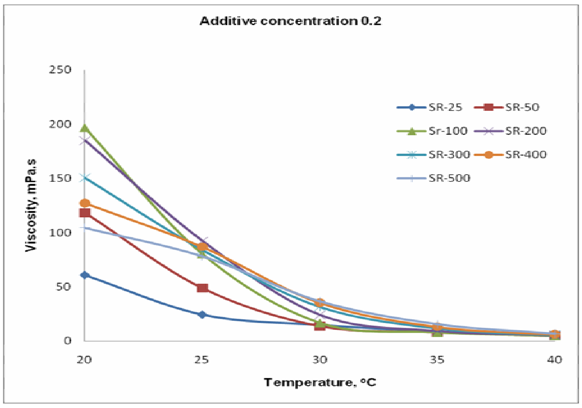

Figure 12. Viscosity vs. Temperature plot of fly ash slurry with additive concentration 0.2%

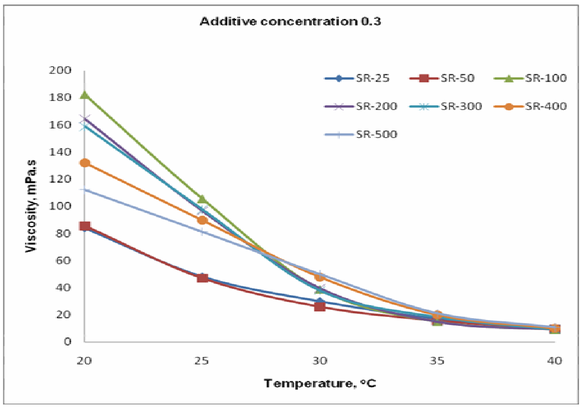

Figure 13. Viscosity vs. Temperature plot of fly ash slurry with additive concentration 0.3%

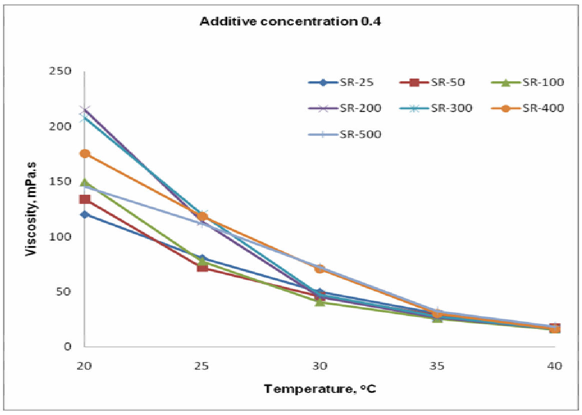

Figure 14. Viscosity vs. Temperature plot of fly ash slurry with additive concentration 0.4%

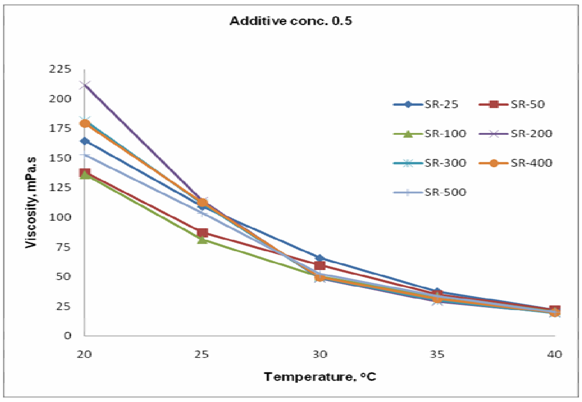

Figure 15. Viscosity vs. Temperature plot of fly ash slurry with additive concentration 0.5%

4.4 Surface Tension

Surfactants are also known as tensides, which are wetting agents and can lower the surface tension of a liquid, allowing easier spreading leading to lower the interfacial tension between solid particles and the liquid. Surfactants are having the property of reducing the surface tension of water by adsorbing at the solid-liquid interface. Surface tension of the six samples in this investigation was measured by Surface Tensiometer (Model: DCAT 11 EC, Data Physics, Germany) and the results are presented in Table 5. From the results it is confirmed that the surfactant used for this study has reduced the surface tension to about 43% to 46% which will lead to smooth flow of fly ash particles in the pipeline.

4.5 Zeta potential

The zeta potential of fine powder fly ash particles and the amount adsorption of the slurry were investigated as well. The zeta potential was measured by using electrophoretic technique by Zeta Sizer-Nano Series (Malvern Instruments, U.K.). From the results it is observed that the zeta potential value of the fly ash slurry was negative without any additive, but it is changed to positive value when surfactant was added to the slurry (Table 5). Addition of the surfactant has modified the surface properties of the fly ash particles keeping the suspension in the stable condition. The zeta potential value is helpful to know the stability of the colloidal suspensions. If this value lies between -30mV and +30mV then the suspension is said to be unstable which means that there will be rapid settling of the particles in the suspension. If this phenomenon occurs, the fly ash particles will either settle down or roll on the pipe bottom during its transportation leading to greater drag friction. If the drag friction will be high the specific energy consumption for the pipeline transport will be high as well as if the transport will be interrupted due to electrical shutdowns or mechanical breakdowns, the solid particles will settle down at the pipe bottom and even it may lead to pipe jam requiring more water (energy) to flush the pipeline to clear the blockage. To overcome this problem we have added a surface-active agent (surfactants) which has lowered the surface tension of the water and at the same time dispersed the fly ash particles in the liquid medium to keep them afloat at least for a period till the materials are transported to its disposal site. From the results it is confirmed that the addition of surfactant has modified the surface properties of the fly ash keeping the suspension in stable condition.

5.0 CONCLUSIONS

The determination of the rheological parameters is important in order to predict the drag reduction behaviour of fly ash slurries during its transportation in pipe lines. Based on the present investigation, the following important conclusions are drawn:

- Fly ash slurries at 30% concentration by weight with addition of a cationic surfactant showed Newtonian and shear thinning fluid behaviour. The viscosity and shear stress values decreased with increasing temperature, decrease being more pronounced at higher temperature.

- It is observed from the surface tension measurements that the addition of the surfactant to the slurry suspension reduced the surface tension of the liquid indicating that there will be substantial reduction in drag friction during its transportation in the pipelines.

- The presence of sizable proportion of finer fly ash particles in the colloidal suspension influenced the stability of the slurry. It was found that the zeta potential value of the fly ash slurry without any additive was -25mV which implied that the suspension was unstable. This was the reason for which the untreated fly ash particles settled down at the bottom of the measuring cup during rheological tests.

- To overcome this problem surfactants were added into the slurry and it was found from the measured data that the zeta potential value changed from minus value to plus value and the zeta potential value for all the suspensions with addition of surfactants exceeded +30mV which confirmed that the suspensions were stable during test measurements.

Acknowledgements

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