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SHORT COMMUNICATION

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Modification of flow properties of concentrated lignite dispersions

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Abstract Concentrated water-based lignite suspensions (pastes) possess unpleasant flow behaviour. Under extrusion-like conditions suspension is rapidly compacted, viscosity rises considerably and flow effectively ceases. Using diluted aqueous solution of carboxymethylcellulose sodium salt as a dispersion medium eliminates this adverse phenomenon and keeps liquid-like flowing of suspension. Moreover, effective dilatant suspension behaviour is transformed to pseudoplastic.

Keywords Carboxymethylcellulose · Lignite paste · Rheological additive · Suspension

Introduction

The main use of lignite still persists in the power plant technology where it is used as a fuel. This utilization of lignite is really wasting of a valuable raw material to say nothing about its relatively low quality as a fuel [1, 2]. Due to the low degree of coalification, lignite can be used even in a natural state in several other areas [3–5]. Among them are various environment protection technologies where lignite serves as a sorbent or agriculture where lignite with high contents of humic substances can be applied as a preparation to support plant production (“organic fertilizer”) and as a soil conditioner. For example, lignite sorbents are used for water treatment, removal of heavy metals (especially mercury), for the sorption of organic pollutants in liquids and nitrogen oxides in air [6–11]. Although in these alternative utilizations lignite can be used in milled natural form, i.e., as a powder or fine “sand”, it is usually more appropriate to prepare bigger particles of at least 1 cm dimension. This is achieved by extruding lignite mass into extrudates of suitable shape. As a processing liquid, water is most simply used. Water contents should not be too high, otherwise the shape of extruded elements is destroyed. Moreover, water is only the processing aid and should be subsequently evaporated which calls for additional costs. The extrusion is therefore made using highly concentrated dispersion of lignite in water to form lignite paste.

During our effort to prepare extrudates of lignite fertilizer severe rheological problems were encountered. Shortly after the start of extrusion the flow resistance of lignite paste sharply increased finally resulting in suspension “freezing” in the machine. Therefore we tackled the problem of rheological characterization of lignite pastes in more detail to resolve such technological rubs. Preliminary results were reported previously [12, 13]; in this study the whole experience is completed and summarized.

Information on flow properties of lignite pastes is really scarce. To the best of our knowledge there are no works studying flow of aqueous lignite pastes. Published works, dealing with both rheology and lignite, are motivated by other problems—dewatering of lignite by compression [14–16] or pumping lignite–water and lignite–oil slurries, which are used in some combustion technologies [17–19]. In its native state lignite may contain about 50% (by weight) or even more of water. Although the proportion of water in its natural state is apparently high it cannot be utilized as a processing aid in our application. It is capped in the inner structure of coal pieces and does not aid paste formation. Fortunately most of the water is so-called free water and can be easily evaporated.

Experimental

South Moravian (Czech Republic) lignite from locality Mikulčice was used in our experiments [2, 20]. It was received in the pre-dried and milled state from the power plant. First, it was dried at 105 °C for 24 h and then sieved. The lignite fraction captured between 0.1 and 0.2 mm sieves was used for subsequent experiments after moisture-equilibration at ambient conditions. Moisture content of lignite material used for the preparation of pastes was thus within the range 5–7%. Lignite particles are very sticky therefore particles smaller than 0.1 mm were present in the used lignite fraction.

Lovosa TS 20 (Lovochemie, Czech Republic), sodium salt of carboxymethylcellulose was used as received. According to the producer's specification, its molecular weight is about 70,000 g/mol. High molecular weight (700,000 g/mol) carboxymethylcellulose (sodium salt, Aldrich) was used in complementary experiments.

Suspensions were prepared by thorough hand mixing of weighted amounts of lignite and the dispersion medium in a beaker. Water-based suspensions were added during mixing along with several drops (0.01–0.02%) of Triton X−100 surfactant (Aldrich, Czech Republic) to improve particles wetting. Carboxymethylcellulose solution was prepared by placing the solid polymer in hot water (70 °C) and then standing overnight at laboratory temperature to complete dissolution. Based on preliminary experiments prepared suspensions were left to stand 1 h after mixing before measurements were performed. Deionized water was used throughout.

Concentration of studied suspensions (pastes) was too high to be tested in rotational rheometer. Attempts to use plate–plate sensor failed due to suspension pulling off the gap during measurement, tearing, and wall slip. Often it was even impossible to make compact layer within the gap before the start of measurement. Therefore, Höppler consistometer (MLW, Germany) was used because it was the only equipment at our disposal able to cope with lignite paste and also especially because it gives flow conditions much closer to the real state during extrusion than rotational rheometer. Loads on consistometer, given in manufacturer documentation in ponds, were recalculated for shear stress according to Höppler's equation, i.e. dividing the load by the cross section of a ball sensor.

Results

In the Höppler consistometer flow behaviour is manifested through the velocity of ball sensor movement in a sample. Viscosity (apparent) is calculated from the velocity of sensor penetration into the sample. Sample flows around the sensor ball and high penetration velocity means low (apparent) viscosity.

Water-based concentrated lignite suspension possesses two-stage flow behaviour, see Figs. 1 and 2 for suspension concentration 50% (w/w). First short stage of relatively fast penetration, i.e. of low apparent viscosity, is followed by much longer second stage during which the penetration decelerates and eventually ceases. Lignite paste thus manifests strong time-dependent flow behaviour characterized by substantial increase in (apparent) viscosity (under constant stress). It should not be considered as an example of true rheopexy but as a result of particular flow arrangement and lignite properties. During the first stage paste is quickly compacted by action of Höppler consistometer sensor (or appropriate extruding element in practice), perhaps part of water is expelled from the interparticle space or even from the particle porous structure. Ability of the paste to flow around the ball sensor is suppressed appreciably, paste becomes stiff, "solidified". Finally, resistance of compacted paste is equilibrated with the consistometer loading force and the flow stops. Apply-

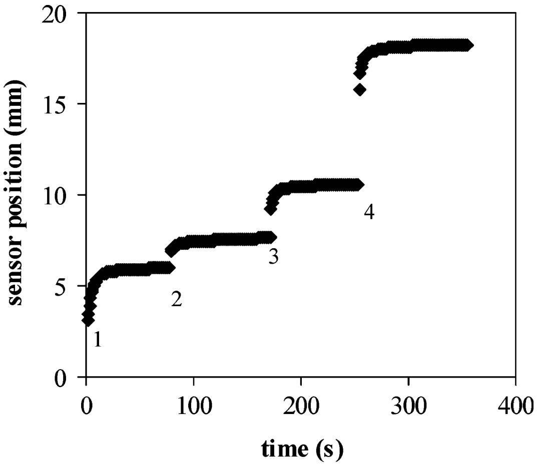

Fig. 1 Example of flow behaviour of water-based suspension containing 50% lignite in Höppler consistometer under increasing load (shear stress): 57.93 kPa (*1*), 115.9 kPa (*2*), 231.7 kPa (*3*), 386.2 kPa (*4*)

ing yet higher load, the flow can be refreshed till the new equilibrium is attained, cf. Fig. 1.

Due to the inherent physical and chemical heterogeneity of the solid phase, its non-inertness to water and high suspension concentration it was very difficult to prepare suspensions and fill consistometer with good reproducibility. Although repeated measurements with suspensions of the same composition were rather scattered, two-stage flow was always evident and reproducibility of relative measured data was quite satisfactory, see Fig. 2. Consistometer data confirmed experience from the technological extrusion and our previous findings [12] very well.

Substantial improvement in flow behaviour of lignitic paste was achieved using aqueous solution of cellulose derivative as dispersion medium. Lovosa TS 20 at 3% (w/w) concentration gave only slight improvement while 5% level was found to be satisfactory. Example of flow behaviour of suspension prepared from the latter solution can be seen in Fig. 3; resulting suspension contained 50% (weight) of lignite and 50% of dispersion medium. Simple sensor penetration behaviour, i.e. time independent giving only single value of (apparent) viscosity, is clearly evident under higher stress. Although here we report results obtained for 50% contents of lignite, measurements were made also with lower concentrations, down to 40%. Whereas water-based suspensions did not show substantial change, in comparison, 50% carboxymethylcellulose-based suspensions gave technologically better flow behaviour (lower apparent viscosity).

To test dependence of flow behaviour on shear stress, experiments with variable consistometer loadings were performed. Before presenting the results a note on data evaluation is added. Data curves showing the two-stage flow were processed in two ways. First, two straight lines were fitted to fast and slow regimes separately, which is indicated in Fig. 2 (but actually applied on absolute not relative consistometer data). From their slopes (s) apparent viscosities in both regimes were calculated using the Höppler consistometer equation

$$\eta = \frac{PK}{s},$$

where η is the (apparent) viscosity, P the consistometer load and K the consistometer constant. Apparent viscosity in fast and slow regime is denoted by η_f and η_s, respectively. Alternatively, the whole data set was fitted with simple nonlinear equation

$$y = \frac{at}{b+t},$$

where y is the position of ball sensor in time t, a and b are the fitting parameters. Derivative of the fitting

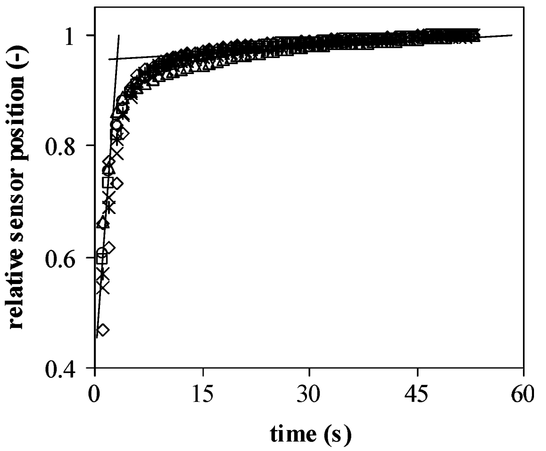

Fig. 2 Relative consistometer data for seven replicates. *Straight lines* illustrate one of the methods used for data evaluation

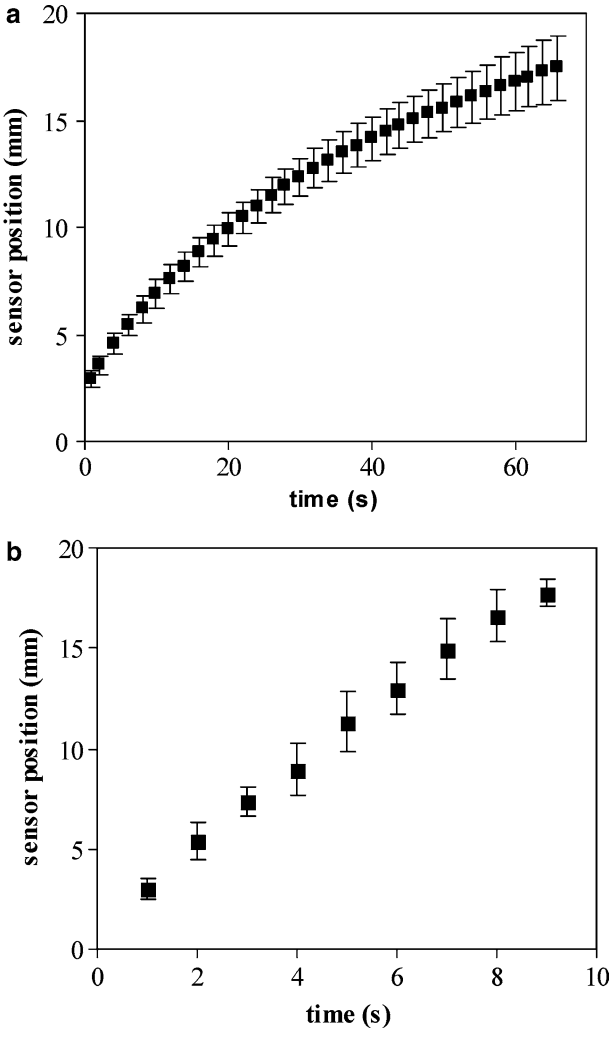

Fig. 3 Flow behaviour of carboxymethylcellulose solution (5%)-based suspension containing 50% lignite in Höppler consistometer under the load (shear stress): **a** 115.9 kPa, **b** 173.8 kPa

Table 1 Flow characteristics of water-based suspension containing 50% lignite under various consistometer load (shear stress)

Stress (kPa)	η_{2s}×10^{-6}(mPa s)	η_{30s}×10^{-8}(mPa s)	η_f ×10^{-6}(mPa s)	η_s×10^{-8}(mPa s)
38.62	3.31 ± 0.684	3.24 ± 1.17	5.23 ± 1.47	5.59 ± 0.351
57.93	4.62 ± 1.14	4.77 ± 0.851	5.55 ± 1.84	6.69 ± 0.377
115.9	13.8 ± 3.62	22.8 ± 2.13	11.6 ± 1.33	25.5 ± 1.63
231.7	21.8 ± 4.18	37.1 ± 11.4	19.7 ± 6.06	37.7 ± 3.73

equation can be easily calculated and used in consistometer equation to obtain apparent viscosity at any measurement time:

$$\eta = \frac{PK(b+t)^2}{ab}.$$

For presentation and comparison purposes apparent viscosity in the 2 and 30 s (η_{2s} and η_{30s}, respectively) calculated from the last equation are given corresponding to the fast and slow flow stage for all samples, respectively.

Results of the processing data from the varying load experiments are given in Tables 1 and 2. Standard deviations (σ) were determined from seven replicates using the well-known relationship [21] $\sigma = a_n R$, where R is range, i.e., difference between the highest and lowest values, and a_n for seven replicates is equal to 0.3698.

Typical apparent viscosities of water-based suspension in fast and slow flow stages differ in about two orders of magnitude regardless of the value of acting stress. Suspension prepared from the carboxymethylcellulose solution shows some two-stage behaviour only under low stress (cf. Fig. 3a where the measured line starts to curve slightly at the end of measurement) and differences in corresponding apparent viscosities, if can be identified, amounts only about half order of magnitude. Data for carboxymethylcellulose-based pastes especially under higher loads could not be fitted with two straight lines, therefore, only one line was fitted on the whole data set; calculated apparent viscosity is given in Table 2.

Even from the time dependent penetration behaviour some conclusions on the shear stress effect could be made. Figure 4a presents dependence of apparent viscosities in both fast and slow regimes, obtained from the double-linear curve fitting, on applied shear stress for water-based lignite suspension. Both values show clear effective shear-thickening or dilatant behaviour. By “effective” it is indicated that actually the flow behaviour is time dependent. On the contrary, (single) apparent viscosity of carboxymethylcellulose-based suspension decreases with increasing stress as illustrated in Fig. 4b.

Table 2 Flow characteristics of carboxymethylcellulose solution (5%)-based suspension containing 50% lignite under various consistometer load (shear stress)

stress (kPa)	η×10^{-6}(mPa s)
115.9	37.5 ± 11.4
154.5	9.09 ± 0.621
173.8	8.83 ± 0.625

The same favourable rheological effect, i.e. suppression of the slow flow stage or flow-freezing, was obtained also with the high molecular weight carboxymethylcellulose, which was used in 1% solution. It even enabled to use smaller consistometer loads because at loads corresponding to those used for low molecular weight Lovosa, the flow was very fast and unmeasurable.

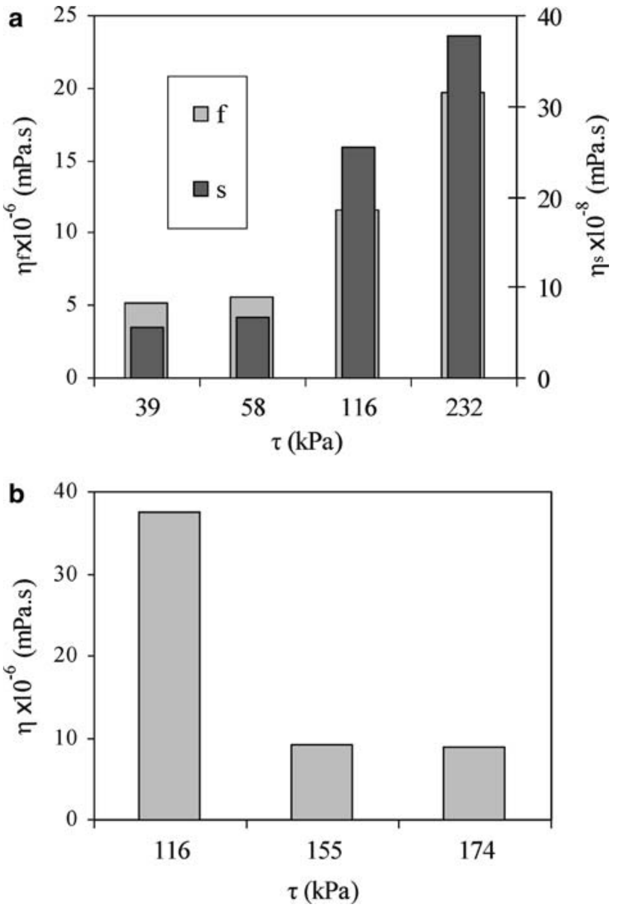

Fig. 4 Dependence of apparent viscosity on shear stress: **a** fast (*f*) and slow (*s*) flow regime of water-based suspension, **b** carboxymethylcellulose solution-based suspension; suspensions contained 50% lignite

Conclusions

Carboxymethylcellulose (its sodium salt) can serve as a suitable rheological additive for processing lignite pastes. Preparing paste using diluted aqueous solution (1–5% depending on the molecular weight) of carboxymethylcellulose instead of water significantly facilitates paste flow and extrusion and suppresses "paste freezing" during extrusion. Stronger effect (at lower solution concentration) was observed for the high molecular weight carboxymethylcellulose. Addition of carboxymethylcellulose also transforms suspension effective dilatant behaviour to pseudoplastic. Carboxymethylcellulose effect can be attributed to some "ball-bearing" action, i.e. slippage of lignite particles on polymeric chains. Cellulose macromolecules may also prevent lignite particles from interacting with water molecules to form tough network. Although carboxymethylcellulose was used as liquid solution showing no recognizable gel character it can be also speculated about forming some gel structure in the lignite–water–carboxymethylcellulose system, which is broken down by stress action and polymeric chains are then free to facilitate slip of lignite particles.

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