# Gelation of Water–Bentonite Suspensions at High Temperatures and Rheological Control with Lignite Addition

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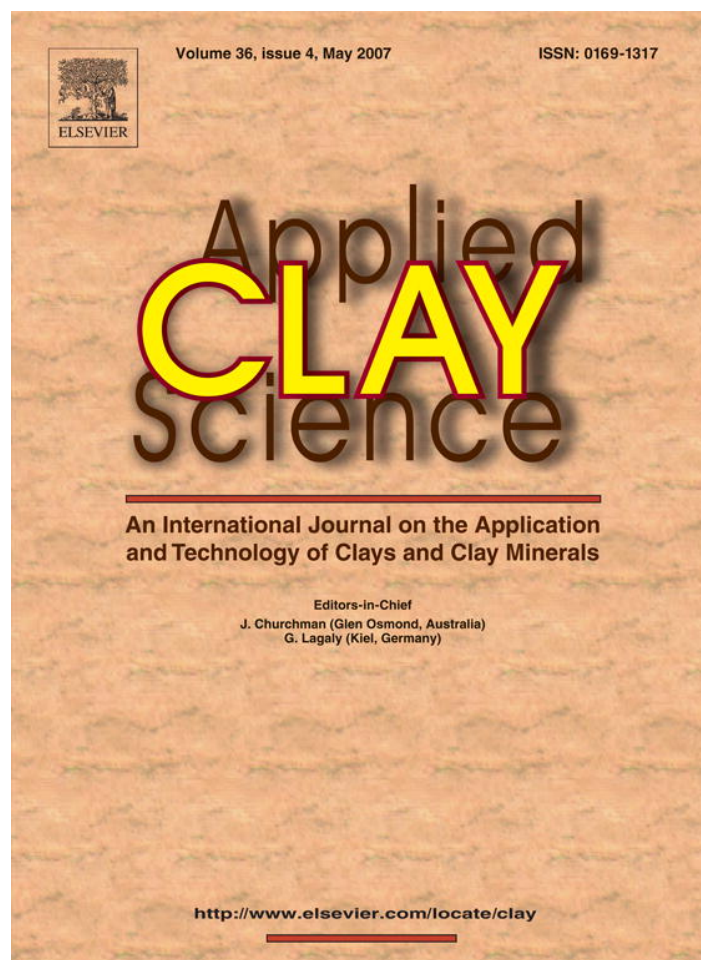
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# Gelation of water–bentonite suspensions at high temperatures and rheological control with lignite addition

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## Abstract

The effectiveness of lignite addition to prevent gelation of 6.42% w/w water–bentonite suspensions exposed to high temperatures has been studied, using twenty six lignites from various basins in Greece with variable organic and inorganic contents at concentrations of 0.5% and 3.0%. The lignite-free bentonite suspensions thickened considerably when heated at 177 °C for 16 h, as was indicated by a two-fold increase of the yield stress, when compared to samples hydrated only at room temperature. However plastic viscosity did not change appreciably. Full flow curves showed a Herschel–Bulkley behavior of all suspensions. Addition of lignite maintained the stability of the suspensions exposed to high temperatures (177 °C) by keeping the yield stress low and did not affect plastic viscosity. Some of the Greek lignites performed equally well with a commercial lignite product and improvements of 80 to 100% of the stability of the suspensions, compared to lignite-free suspensions, have been found. Lignite addition also lowered yield stresses for the hydrated samples. No specific trends have been identified between the effectiveness of lignites to stabilize bentonite suspensions and their humic and fulvic acids and humins content. However, those lignites with highest humic and fulvic acid contents have maximum stabilization capacity. Similarly, no specific trends have been observed between the stabilization capacity of lignites and their inorganic components such as oxygen and ash content and also with the cation exchange capacity. The effectiveness of the Greek lignites to stabilize bentonite suspensions is very high and the minor differences in the efficiency of the different lignites cannot be attributed solely to any specific component.
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## 1. Introduction

Drilling fluids are significant elements for oil well drilling particularly for very deep wells where excessively high temperatures and pressures are encountered. Additionally, the increasing number of horizontal wells has put stringent requirements for stable drilling fluids having strict specifications. High temperatures are also encountered during geothermal drilling with recent reports revealing static temperatures in excess of 500 °C in a geothermal well (Saito et al., 1998; Saito and Sakuma, 2000). Drilling fluid research has produced

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a range of drilling fluids that are capable of performing these formidable tasks in these difficult environments. Among the properties that drilling fluids must posses are appropriate viscosity with shear thinning behavior and finite yield stresses for suspending mixing material, usually barite, and for transferring drill cuttings to the surface.

It is well known that above about 120 °C, and in conditions of high salinity, colloidal systems composed of bentonite begin to thicken considerably (Gray and Darley, 1980; Bleler, 1990; Elward-Berry and Darby, 1992) but the mechanism of action is not completely understood (Alderman et al., 1988; Luckham and Rossi, 1999). Frequently, in real production systems these fluids remain exposed to high temperatures for long periods where they form strong gels, imparting thus excessive pressure drop when flowing. To overcome these problems in the past, fluids having oil as the main liquid-phase were used because they were stable at these high temperatures. However due to environmental, logistical and cost considerations, use of oil-based fluids (even the more recently formulated synthetic oil-based drilling fluids) is often not possible. Therefore, water-based drilling fluids containing bentonite are used in these difficult environments. Various additives are then used to enable these fluids to withstand these high temperatures (Clark, 1994).

For temperatures higher than 100 °C bentonite suspensions with no additives exhibit a small decrease in plastic viscosity but a drastic increase in yield stress. However, bentonite suspensions containing anti-flocculation additives show a decrease in both rheological parameters for temperatures as high as 177 °C (Hiller, 1963; Annis, 1967; Gray and Darley, 1980; Alderman et al., 1988; Briscoe et al., 1994; Santoyo et al., 2001). Use of alternative clay materials like sepiolite and loughlinite has been reported but the suspensions have inferior filtration properties and cannot replace bentonite suspensions (Carney and Meyer, 1976; Bannerman and Davis, 1978; Zilch et al., 1991; Serpen, 2000).

The additives used in bentonite suspensions are usually anionic polyelectrolytes which are thought to bind on the bentonite particle surface, prohibiting agglomeration of clay particles and maintaining the stability of the suspensions (Gray and Darley, 1980; Rabaioli et al., 1993; Zhang and Yin, 2002). The additives used include modified, or non-modified, natural compounds like lignosulfonate complexes with various metals, tannins, humic acids, lignite and modified lignite and synthetic polymer products (Gray and Darley, 1980; Rabaioli et al., 1993; Patel, 1995; Burrafato et al., 1995). Previous work on bentonite suspensions at room temperature has shown that anionic organic molecules are adsorbed on the clay surfaces imparting them a more negative charge, thereby increasing their mutual repulsion and maintaining the stability of the suspensions (Beckett and Le, 1990; Sondi et al., 1996; Tombácz et al., 1999).

Various forms of lignite, often complexed with metals, have been used in the past to maintain the stability of drilling fluids at high temperatures (Hilscher and Clements, 1982; Nyland et al., 1988; Oort et al., 1997). Use of lignites in drilling fluids usually requires an alkaline additive such as NaOH to increase its solubility, with the pH of the system ranging from 9.0 to 11.5 (Clark, 1994). The type of lignite used in drilling fluids is leonardite and the factors thought to enhance lignite performance are oxygen content and the content of humic and fulvic acids (Patel, 1995). Gavrilof et al. (1999) demonstrated that lignites with high concentration of humic acids, low resin content, low ash content, and low sulphur content provided maximum rheological stability and filtration control of drilling fluids at high temperatures. Although there is evidence for the effectiveness of leonardite to maintain the stability of bentonite suspensions, there are no studies readily available on the mechanism of its activity or comparative studies on the effectiveness of conventional lignites.

Greece has several lignite deposits of various sizes, with some of them in insufficient reserves to justify exploitation for power generation (Koukouzas et al., 1997; Papanicolaou et al., 2004) and various studies have been undertaken to identify non-electric uses of lignite. This work presents the results of such a study which aimed a) to study the suitability of various Greek lignites as additives to control gelation of water-bentonite suspensions at high temperatures and b) to identify the components of lignite that impart the good performance as rheological control agents.

## 2. Experimental methods

The experimental procedures and preparation methodology have been described elsewhere (Kelessidis et al., in press). A brief description will be given here. The bentonite used is an industrial product from Greece (Zenith©) used in oil well drilling, provided by S&B Industrial Minerals SA. The bentonite consists mainly of montmorillonite (>90%) and minor quartz calcite dolomite and brookite. The chemical analysis is given in Table 1. Most of the material (>90%) is finer than 75 μm to meet API 13A (1993) specifications. Particle size analysis of the bentonite powder is given in Fig. 1. Lignite samples from different lignite basins were provided by the Greek Institute of Geology and Mining Exploration (IGME) and are coded by the area of exploitation (Table 2).

Table 1
Chemical analysis of Zenith bentonite

| Component | Quantity (%) | Component | Quantity (%) |
|---|---|---|---|
| $Na_2O$ | 2.01 | $Fe_2O_3$ | 5.07 |
| MgO | 4.02 | $Al_2O_3$ | 20.25 |
| $K_2O$ | 0.65 | $SiO_2$ | 59.31 |
| CaO | 5.92 | $P_2O_5$ | 0.00 |
| $TiO_2$ | 0.68 | LOI[a] | 1.83 |
| MnO | 0.08 | | |
| Sum | | | 99.83 |

[a] Loss of ignition.

The cation exchange capacity (CEC) and the moisture of the lignites are also listed in Table 2. Since the humic content of the lignite is thought to be the component primarily responsible for the effectiveness of lignite (Patel, 1995; Gavrilof et al., 1999), the contents of humic acids, fulvic acids and of humin were also determined according to Swift (1996). The total inorganic material (ash) varied between 3% and 30% and the oxygen content, determined according to ASTM (1978), was found ranging, on a dry basis, between 20% and 35%.

Bentonite concentration in deionized water was 6.42% w/w (API 13A, 1993) forming the base fluid, coded A. Lignite was added at concentrations of 0.5% and 3% w/w. Accordingly, the suspensions were coded A+I, where I is the lignite code. A commercial lignite additive (Caustilig®) coded Γ was supplied by SWACO and was used as control additive.

Bentonite and commercial lignite were used as received. The Greek lignite samples were dried at 105 °C and ground to pass a 75-μm sieve. The lignite powder was subsequently treated with 1 M NaOH, a process called caustisization, to increase the solubility of lignite in the fluid and to adjust the pH so as to become alkaline (Russell and Patel, 1987; Patel, 1995; Gavrilof et al., 1999). The caustisized lignites were then dried at 70 °C for 2 days and were ground to a particle size less than 75 μm.

The suspensions were prepared according to API 13A (1993). Two types of suspensions were used: a) suspensions sealed in a container for 16 h at room temperature (hydrated samples), and b) suspensions placed in an aging cell,
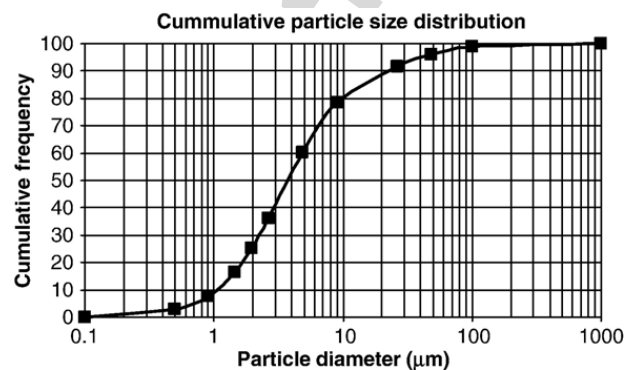


Fig. 1. Cumulative particle size distribution for Zenith bentonite.

Table 2
Location, lithotypes, moisture and CEC of lignites used in this study

| Code name | Origin | Lithotypes | Moisture % | CEC meq/100 g lignite |
|---|---|---|---|---|
| Γ | M-I SWACO | Commercial lignite product | 0.7 | 81.5 |
| TH1 | Thessaly | Peat with clay particles | 67.1 | 88.8 |
| TH2 | Thessaly | Peat with clay particles | 56.0 | 88.1 |
| TH3 | Thessaly | Matrix brown coal, clay-rich, friable | 63.2 | 91.1 |
| TH4 | Thessaly | Matrix brown coal, with plant remnants | 46.5 | 109.8 |
| TH5 | Thessaly | Matrix brown coal, with plant remnants | 29.7 | 82.3 |
| TH6 | Thessaly | Xylite brown coal | 31.0 | 78.7 |
| TH7 | Thessaly | Xylite brown coal | 37.4 | 103.0 |
| TH8 | Thessaly | Matri brown coal, xylitic, with plant remains | 30.0 | 77.6 |
| MT1 | Macedonia | Mixed peat, clay-rich, black colour | 22.3 | 37.8 |
| MT2 | Macedonia | Mixed peat, clay-rich, black colour | 34.3 | 71.8 |
| MT3 | Macedonia | Mixed peat, clay-rich, black colour | 25.4 | 38.7 |
| MT4 | Thrace | Matrix brown coal, stratified, clay-rich, friable | 19.7 | 50.2 |
| MT5 | Thrace | Matrix brown coal, stratified, clay-rich, cluster bands containing xylitic fragments | 20.6 | 5.5 |
| MT6 | Thrace | Matrix brown coal, stratified, clay-rich, cluster bands containing xylitic fragments | 19.8 | 11.1 |
| MT7 | Thrace | Matrix brown coal, stratified, clay-rich, cluster bands containing xylitic fragments | 18.7 | 38.8 |
| MT8 | Thrace | Matrix brown coal, stratified, cohesive at places, presence of micas | 19.2 | 47.3 |
| ΠΠ1 | Peloponissos | Matrix brown coal, stratified, xylitic at places | 14.5 | 102.1 |
| ΠΠ2 | Peloponissos | Matrix brown coal, xylitic | 18.3 | 101.2 |
| ΠΜ1 | Peloponissos | Matrix brown coal, stratified, clay-rich | 17.4 | 96.3 |
| I1 | Epirus | Matrix brown coal | 18.9 | 81.7 |
| I2 | Epirus | Matrix brown coal, clay rich | 14.1 | 80.6 |
| ΚΠ1 | Crete | Subbituminous, lustreous appearance | 9.4 | 64.0 |
| ΚΠ2 | Crete | Subbituminous, mat/lustreous appearance | 5.7 | 57.3 |
| ΚΠ3 | Crete | Brown matrix coal, layered at places, mat/glossy | 4.7 | 43.2 |
| ΚΠ4 | Crete | Organic matter bearing clay, layered, cohesive in some places | 4.2 | 27.3 |
| ΚΠ5 | Crete | Mixture of ΚΠ1 and ΚΠ2 at a ratio 1:2 | 6.9 | 67.4 |
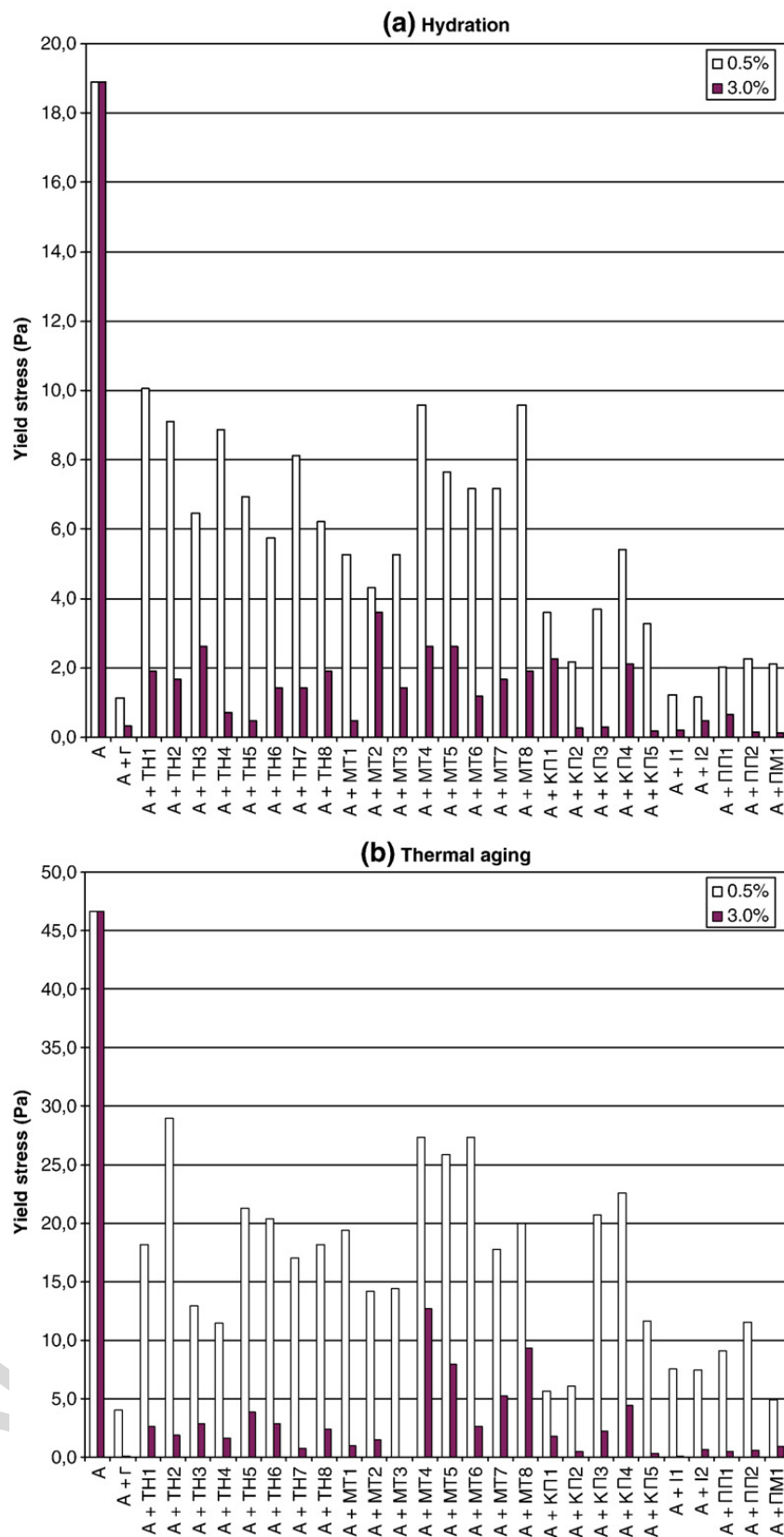
Fig. 2. Variation of yield stress of 6.42% bentonite dispersions at 0.5% and 3.0% lignite concentrations. (a) Hydrated samples, (b) thermally aged samples.
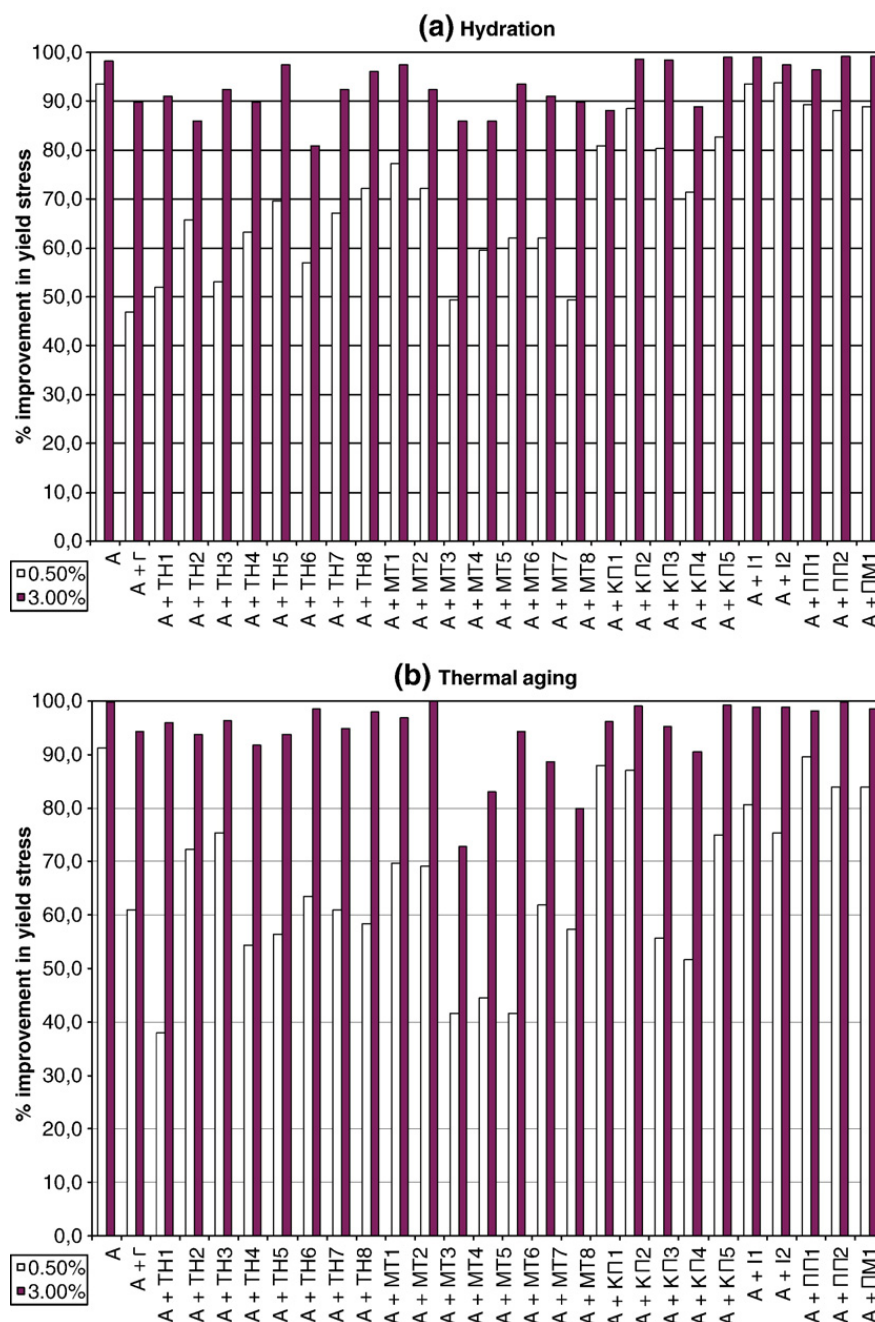
Fig. 3. Improvement of yield stress of 6.42% bentonite dispersions at 0.5% and 3.0% lignite concentrations, (a) after hydration (b) after thermal aging.

pressurized at 7 bar, and then in an oven at 177 °C for 16 h (thermally aged samples) (Gray and Darley, 1980; API 13I, 2000). Thermal aging simulates the environment which is encountered when the drilling fluid is left static for long periods in high temperature wells and represents the most severe high temperature testing. After the aging period, the samples were brought to room temperature, and then were transferred to the container to perform the rheological measurements at room temperature.

A six-speed rotational Couette-type viscometer (Fann 35S), with an inner cylinder diameter of 1.7245 cm and an outer rotating cylinder diameter of 1.8415 cm, giving a diameter

ratio $\delta = 1.06785$, was used to measure the rheological properties of the suspension. Drilling fluid industry specifies for the use of the high rotational speeds (600 and 300 rpm) of the rotating viscometer used for this purpose (for e.g. Fann35S), to compute the two rheological parameters of the Bingham plastic model (Bourgogne et al., 1991; API 13B-1, 2003; API 13D, 2003). This approach, although questioned many times because not only it does not take into account readings from the full shear rate range and in particular at low shear rates (for e.g. Hemphill et al., 1993; Clark, 1995; Maglione et al., 2000; Kelessidis et al., 2005; Kelessidis and Maglione, 2006) but also because it uses Newtonian shear

rates for the particular model, computed as 1021 s$^{-1}$ and 511 s$^{-1}$ at 600 and 300 rpm respectively, instead of using true shear rates in the viscometer (Kelessidis et al., 2005; 2006), it is standard drilling industry practice for many years and industry has been slow to accept proposed changes (Bailey and Peden, 2000; Zamora and Power, 2002).

The computed parameters are thus (Bourgogne et al., 1991), the plastic viscosity, (PV)

$$PV = (\theta_{600} - \theta_{300}) \quad (mPa^*s) \quad (1)$$

and the yield stress (or yield point) of the fluid, YP

$$YP = 0.4788(\theta_{300} - PV) \quad (Pa) \quad (2)$$

where $\theta$ is the dial reading of the instrument.

Rheological data were also obtained with a continuously varying rotational speed Grace M3500 viscometer with similar geometry and dimensions as the Fann35S instrument, at room temperature. The data of the full flow curves were fitted to the Herschel–Bulkley rheological model (Herschel and Bulkley, 1926)

$$\tau = \tau_y + K(\dot{\gamma})^n \quad (3)$$

where $\tau$ is the shear stress, in (Pa), $\tau_y$ is the Herschel–Bulkley yield stress of the fluid, in (Pa), $K$ is the flow consistency index, in (Pa*s$^n$) and $n$ is the flow behavior index.

## 3. Results and discussion

The values of the yield stress after the addition of lignites are shown in Fig. 2a for the hydrated suspensions and in Fig. 2b for the thermally aged suspensions. For the hydrated suspensions, the yield stress decreases significantly when lignite is added at both concentrations, with the extent of decrease varying according to the lignite used. The commercial lignite sample but also few Greek lignites (KΠ2, I1, I2) yielded very small values of yield stress. For the aged suspension (Fig. 2b) of pure bentonite (sample A), the yield stress is very high, more than double of the hydrated sample, owing to the gelation effect that occurs when bentonite suspensions are exposed to high temperatures. Addition of lignites and then thermal aging stabilizes the suspensions, with the stabilization effect being more significant with 3% lignite addition, for most of the lignites tested. Several lignites have shown an almost liquefying effect reducing the yield stress of the aged suspensions to very small values after 3% addition (sample Γ and the Greek lignites KΠ2, KΠ5 and I1). The majority of lignites maintain yield stress less than 5.0 Pa after addition of 3% lignite.

The percent improvement in performance of the bentonite suspensions is defined as the ratio of the difference between the specific rheological property of the pure bentonite suspension and the suspension with
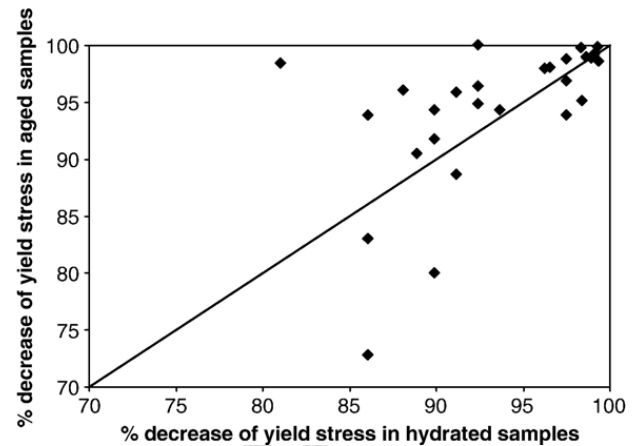


Fig. 4. Comparison of decrease of yield stress of hydrated and aged samples for suspensions with 3% lignite.

bentonite and lignite over the value of the rheological property of the bentonite suspension. The improvement for the yield stress is shown in Fig. 3a for the hydrated samples and in Fig. 3b for the thermally aged samples. For the hydrated samples, the percent improvement varies from 40% to over 90% after addition of 0.5% lignite. Addition of 3% lignite improved the yield stresses by more than 80% for the majority of the lignite samples, with some lignites yielding improvement of almost 100%. In the thermally aged suspensions (Fig. 3b), addition of 0.5% lignite results in an improvement of yield stress between 40 and 90% while 3% addition results in 70 to 100% improvement, with the majority of the samples yielding improvement over 90%. It is worth noticing that for both hydrated and thermally aged samples in suspensions containing 3% lignite, some of the Greek lignites had comparable or even better performance than the commercial lignite.

The improvement of yield stress of the aged samples is plotted against the improvement of yield stress of the hydrated samples in Fig. 4. The results show that the improvement for most of the aged samples with lignite appears to be of similar magnitude to the improvement for the corresponding hydrated samples. This suggests that each lignite type may affect the yield stress of the suspension in the same way, irrespectively of the methodology of sample preparation (hydrated or aged).

The plastic viscosity of the bentonite and the bentonite–lignite suspensions, at two lignite concentrations, after hydration and after thermal aging are shown in Fig. 5a and b respectively. For the hydrated samples (Fig. 5a) and the majority of the lignite types, the effect of lignite addition on plastic viscosity is insignificant at both lignite concentrations. For the thermally aged samples (Fig. 5b), addition of most types of lignites at both concentrations results in an increase of plastic viscosity,
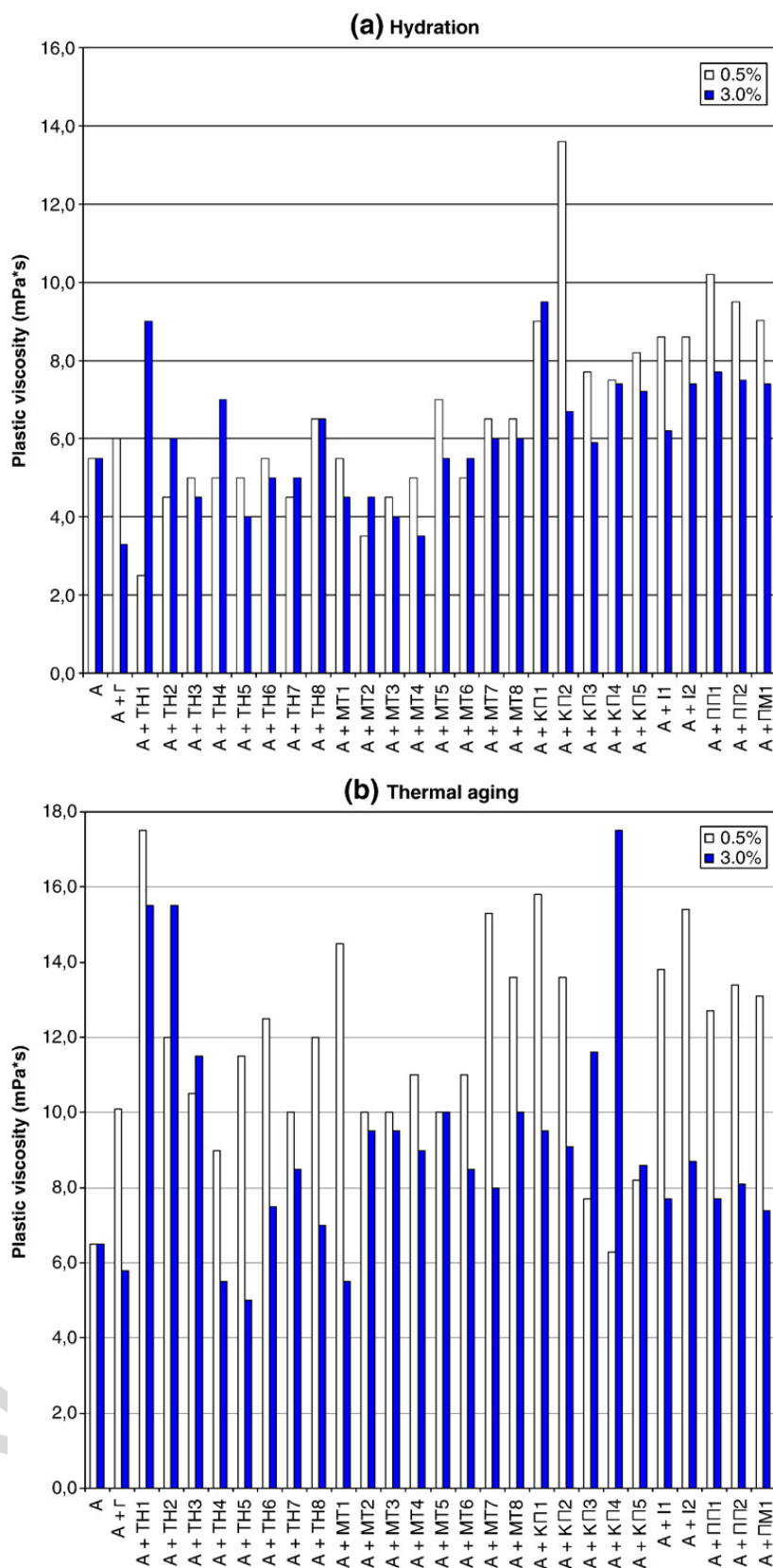
Fig. 5. Variation of the plastic viscosity of 6.42% bentonite dispersions at 0.5% and 3.0% lignite concentrations, (a) after hydration (b) after thermal aging.
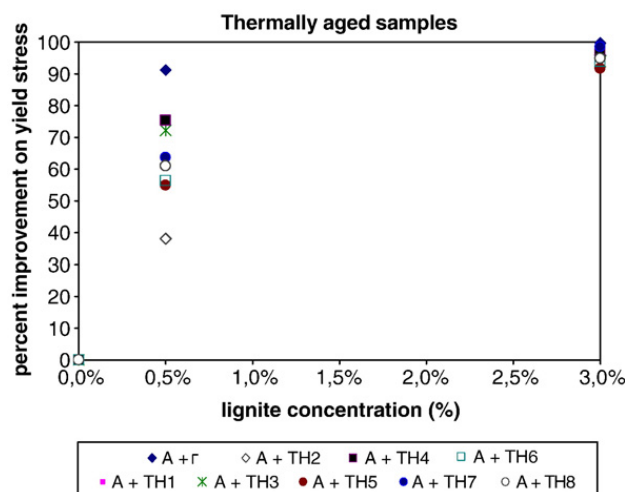
Fig. 6. Variation of percent improvement of the yield stress of thermally aged suspensions with amount of added lignite, for lignite types from one region (Thessaly).

although no specific trend is observed. The increase in plastic viscosity implies an increase of the amount of dispersed smectite particles.

The data obtained for plastic viscosity and yield stress demonstrate that lignite addition improves the rheological properties of the thermally aged bentonite suspensions by keeping the smectite particles separated and prohibiting agglomeration, whereas gelation is observed when no lignite is added in the suspension. The effect is more significant at 3% lignite concentration compared to 0.5% lignite concentration, for all lignite types studied. In Fig. 6 the improvement on the yield stress is plotted vs lignite concentration for various lignite types, for lignites from one of the regions studied, with similar results obtained for
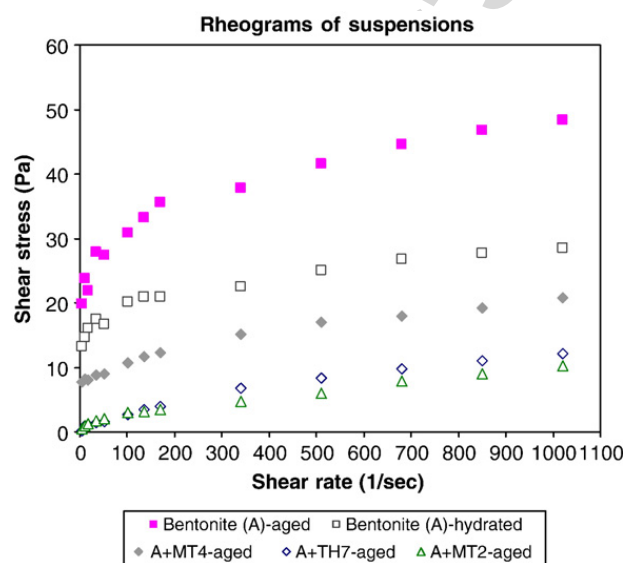
Table 3
Herschel–Bulkley rheological parameters for bentonite and bentonite–lignite samples

| Sample | $\tau_y$ | $K$ | n | $R_c^2$ |
|---|---|---|---|---|
| | (Pa) | (Pa * s$^n$) | (−) | (−) |
| Bentonite (A)-hydrated | 8.50 | 3.40 | 0.26 | 0.988 |
| Bentonite (A)-aged | 11.30 | 5.91 | 0.26 | 0.989 |
| Bentonite + TH7, aged | 0.40 | 0.09 | 0.70 | 0.994 |
| Bentonite + MT2, aged | 0.68 | 0.07 | 0.70 | 0.994 |
| Bentonite + MT4, aged | 6.39 | 0.45 | 0.50 | 0.995 |

lignites from the other regions. The improvement can be significant for some of the lignite types, even from the same region but linearity or non-linearity of the correlation cannot be assessed only from the three points used.

Fig. 7 shows the rheograms, obtained with the Grace viscometer for selected samples. The curves are typical of yield-pseudoplastic materials, as it has been reported for the rest of the suspensions (Kelessidis et al., 2005). The gelation of the pure bentonite suspensions after high temperature exposure is clearly seen, because the shear stresses of the aged sample, at all shear rates, are approximately twice as large as the shear stresses of the hydrated bentonite sample. The high shear rates region display a fairly linear behavior, but strong non-linearity is observed for shear rates less than approximately 200 s$^{-1}$. Addition of 3% lignite followed by thermal aging of the suspensions results in much smaller shear stresses, smaller than both the hydrated and the thermally aged bentonite samples, at all shear rates. All data could be fitted well with the Herschel–Bulkley rheological model and the values of the rheological parameters are given in Table 3 for the samples shown in Fig. 7, where $R_c^2$ is the coefficient of determination.

The effectiveness of the lignite as additive to prevent gelation of bentonite particles has been partly attributed



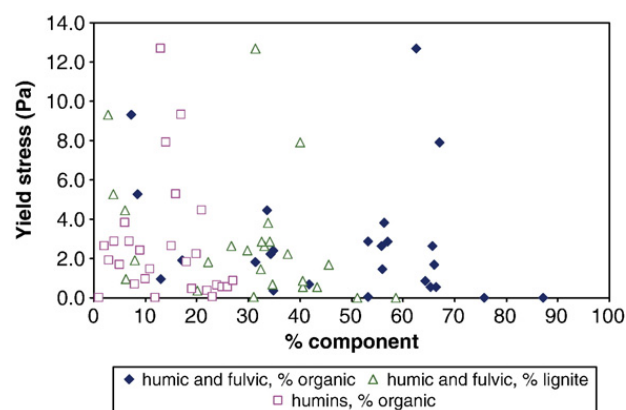Fig. 7. Full rheograms of bentonite and bentonite–3% lignite suspensions.



Fig. 8. Variation of yield stress with organic components of lignite for the bentonite–3% lignite suspensions, after being thermally aged.

to the humic acids present in lignite as well as to high oxygen content (Patel, 1995; Gavrilof et al., 1999). An attempt was thus made to correlate these constituents of lignites with the yield stress of the thermally aged suspensions, because the yield stress is the property that signifies gelation of bentonite particles at high temperatures. In Fig. 8 the variation of the yield stress with the content of organic components is shown. Humic and fulvic acids concentration in the lignites tested varied between 8% and 85% of the total organic and between 5% and 60% of lignite mass, while humin concentration varied between 0% and 30% of total organic matter.

Low yield stresses of thermally aged samples indicate stabilization of the suspensions and most of the results of Fig. 8 show this stabilizing effect. There is not, however, any specific trend with respect to any of the organic components tested, humic and fulvic acids and humins. Most suspensions with low yield stress are those containing lignites with fairly high concentrations of humic and fulvic acids, ranging between 50 and 70%, although there are exceptions to this trend. Moreover it is clear that those lignites with maximum humic and fulvic acids content have maximum stabilization capacity for the bentonite suspensions. Also, almost all lignites when added to the suspensions have decreased the yield stresses of the aged samples by more than 90% with respect to the pure bentonite suspensions (Fig. 8). The results also showed no direct correlation of the $O_2$ content and of the ash content of the lignites tested with the decrease of the yield stresses of the aged samples, contrary to results of previous work (Patel, 1995). Low yield stresses were obtained for samples with lignites with cation exchange capacity generally larger than 50 meq/100 g, although again, no specific trends are observed.

Humic compounds have been shown to stabilize clay suspensions (Tombácz et al., 1988; Goldberg and Foster, 1990; Frenkel et al., 1992; Heil and Sposito, 1993a,b; Kretzschmar et al., 1997; Tombácz et al., 1999) reducing primarily the yield stress, with all these works conducted at low temperatures. Humic acids are negatively charged polyelectrolytes mainly due to ionization of carboxylic and to lesser extent of phenolic groups (Jones and Bryan, 1998; Liu and Gonzalez, 1999; Ramos-Tejada et al., 2003). They contain both hydrophilic and hydrophobic moieties behaving like surfactants (Rebhun et al., 1996; Bilanovic et al., 2004) and are characterized as a group of natural high molecular aromatic acids with over 80% of their oxygen content in carboxylic and phenolic hydroxyls (Butuzova et al., 1998; Schulten and Gleixner, 1999). Humic acid molecules become more negatively charged with increasing pH and medium ionic strength (Tombácz et al., 2004). Their effect depends on clay concentration at basic pH

(Ramos-Tejada et al., 2001). The exact mechanism, of adsorption of humic acids on smectites, which could explain the stabilization effect, is not known with certainty. They may adsorb only on the edges of smectite particle thus providing steric plus electrostatic stabilization of mineral particles (Tombácz et al., 1988, 1999) or on the faces as well through a mechanism of coordinative and hydrophobic interaction (Oochs et al., 1994; Ramos-Tejada et al., 2001; Zbik and Horn, 2003).

A potential third mechanism of stabilization could be that humic acids promote metal adsorption (from suspension) on the mineral surfaces aiding thus in metal complexing between the faces of clay particles, as it has been observed for kaolinite (Arias et al., 2002). Fulvic acid does not adsorb on sodium montmorillonite particles (Sondi et al., 1996) whereas humic acids show pH dependent adsorption on sodium montmorillonite, decreasing at higher pH (Liu and Gonzalez, 1999). Humic compounds are also considered as cementing compounds in aggregates but may also disperse aggregates within a certain concentration range (Tarchitzky and Chen, 2002; Visser and Callier, 1998; Bilanovic et al., 2004).

It can therefore be considered that humic acids or total humic and fulvic acids content present in lignites are important factors, which control the stability of the bentonite suspensions when exposed to high temperatures. However, further work is needed on the subject to fully identify the component or components in the lignite responsible for this. For example, use of pure organic components as additives to bentonite suspensions may help isolate possible synergetic effects from other lignite components. Similarly, multivariate analysis of the results could help to identify any possible combined effect of the lignite components.

## 4. Conclusions

The effectiveness of adding lignites at two different concentrations in 6.42% w/w water-bentonite suspensions to avoid gelation at high temperatures has been investigated using Greek lignite samples from 26 different deposits. The flow curves of some of the suspensions show that the Herschel–Bulkley model properly describes experimental data.

Water-bentonite suspensions thicken substantially upon exposure to high temperatures developing high yield stress, whereas there is only a small effect on plastic viscosity. Addition of lignites at 0.5% and 3.0% prior to thermal aging at 177 °C for 16 h prevented the observed gelation of the bentonite suspensions, particularly at 3% lignite concentration. Most of the Greek lignites tested performed equally well as a commercial

lignite product used for comparison but variations among the different Greek lignite samples have been observed. The decrease of the yield stress for the thermally aged samples ranged from 45 to 90% for 0.5% lignite addition and from 75 to 100% for 3.0% lignite addition. Addition of most lignites resulted in a slight increase in plastic viscosity but no specific variation has been identified with respect to lignite concentration.

Addition of lignites in the hydrated samples also lowered the yield stress of the hydrated suspensions. Decrease of the yield stress ranged between 40 and 95% for 0.5% lignite addition and from 80 to 100% for 3.0% lignite addition. The plastic viscosity was not affected by lignite addition for most of tested samples, with some of the samples showing a slight increase in plastic viscosity.

The effectiveness of the Greek lignites to prevent gelation of bentonite suspensions does not seem to be linked directly to specific organic or inorganic lignite components such as humic and fulvic acids and humins, oxygen content, ash content and cation exchange capacity of lignites, contrary to previous works. The lack of a specific correlation may be looked for in the contradictory effect of the different components. Overall, most of the lignites tested performed successfully and it is considered that the observed efficiency variations were not significant enough to single out the most relevant component for their effectiveness.

## Acknowledgements

## References

Alderman, N.J., Gavignet, A.A., Guillot, D., Maitland, G.C., 1988. High temperature, high pressure rheology of oil based muds. SPE 18035 Annual Tech. Conf. and Exhibition, Houston, TX, October 2–5.

American Petroleum Institute, API Spec. 13A, 1993. Specification for drilling fluid materials.

American Petroleum Institute, API Spec. 13I, 2000. Recommended practice standard procedure for laboratory testing drilling fluids.

American Petroleum Institute, API Spec. 13B-1, 2003. Recommended practice for field testing water based drilling fluids.

American Petroleum Institute, API Spec. 13D, 2003. Recommended practice on the rheology and hydraulics of oil-well drilling fluids.

American Society for Testing Materials, 1978. Annual book of ASTM standards. American Society for Testing Materials, Philadelphia, PA.

Annis, M.R., 1967. High temperature properties of water based drilling fluids. J. Pet. Technol. 21, 1074–1080.

Arias, M., Barral, M.T., Mejuto, J.C., 2002. Enhancement of copper and cadmium adsorption on kaolin by the presence of humic acids. Chemosphere 48, 1081–1088.

Bailey, W.J., Peden, J.M., 2000. A generalized and consistent pressure drop and flow regime transition model for drilling hydraulics. SPE Drill. Complet. 15 (1), 44–56.

Bannerman, J.K., Davis, N., 1978. Sepiolite muds for hot wells, deep drilling. Oil Gas J. 76, 144–150 (Feb.).

Beckett, R., Le, N.P., 1990. The role or organic matter and ionic composition in determining the surface charge of suspended particles in natural waters. Colloids Surf., A Physicochem. Eng. Asp. 44, 35–49.

Bilanovic, D.D., Spigarelli, S.A., Kroeger, T.J., 2004. On formation and decomposition of bentonite–humic and caolinite–humic aggregates in diluted suspensions. Proceedings Eurosoil 2004. www.nondenkunde2.uni-freiburg.de/eurosoil.

Bleler, R., 1990. Selecting a drilling fluid. J. Pet. Technol. 42, 832–834.

Bourgogne, A.T., Chenevert, M.E., Millheim, K.K., Young Jr., F.S., 1991. Applied Drilling Engineering. SPE Textbook Series, vol. 2. Society of Petroleum Engineers, Richardson, TX.

Briscoe, B.J., Luckham, P.F., Ren, S.R., 1994. The properties of drilling muds at high-pressures and high-temperatures. Philos. Trans. R. Soc. Lond. Ser. A: Math. Phys. Sci. 348 (1687), 179–207.

Burrafato, G., Miano, F., Carminati, S., Lockhart, T.P., 1995. New chemistry for chromium free bentonite drilling fluids stable at high temperatures. SPE 28962 paper presented at the SPE Intern. Symposium on Oilfield Chemistry, San Antonio, TX, USA, 14–17 Feb.

Butuzova, L., Krzton, A., Bazarova, A., 1998. Structure and properties of humic acids obtained from thermo-oxidized brown coal. Fuel 77 (6), 581–584.

Carney, L.J., Meyer, R.L., 1976. A new approach to high temperature drilling. SPE 6025 Annual Tech. Conf. New Orleans, March 6.

Clark, R.K., 1994. Impact of environmental regulations on drilling fluid technology. J. Pet. Technol. 46 (9), 804–809.

Clark, P.E., 1995. Drilling mud rheology and the API recommended measurements, paper SPE 29543 presented at the Production Operations Symposium, Oklahoma City, OK, April 2–4.

Elward-Berry, J., Darby, J.B., 1992. Rheologically stable, nontoxic, high-temperature water-base drilling fluid. SPE 24589 Annual Tech. Conf. and Exhibition, Washington, October 4–7.

Frenkel, H., Fey, M.V., Levy, G.J., 1992. Organic and inorganic anion effects on reference and soil clay critical flocculation concentration. Soil Sci. Soc. Am. J. 56, 1762–1766.

Gavrilof, B.M., Koledin, D.M., Gorlof, E.G., Daduka, L.A., Moika, U.N., 1999. Use of Russian lignites in production of drilling fluids, Khimiya Tverdovo Topliva, Mar–Apr, pp. 75–79 (in Russian).

Goldberg, S., Foster, S., 1990. Flocculation of reference clays and arid-zone soil clays. Soil Sci. Soc. Am. J. 54, 714–718.

Gray, H.C.H., Darley, G.R., 1980. Composition and properties of oil — well drilling fluids, Gulf Pub. Co.

Heil, D., Sposito, G., 1993a. Organic-matter role in illitic soil colloids flocculation. 1. Counter ions and pH. Soil Sci. Soc. Am. J. 57, 1241–1246.

Heil, D., Sposito, G., 1993b. Organic-matter role in illitic soil colloids flocculation. 2. Surface-charge. Soil Sci. Soc. Am. J. 57, 1246–1253.

Hemphill, T., Campose, W., Pilehvari, A., 1993. Yield–power law model more accurately predicts mud rheology. Oil Gas J. 45–49 (Aug. 23).

Herschel, W.H., Bulkley, R., 1926. Konsistenzmessungen von Gummi-Benzollosungen. Kolloid-Z. 39, 291–300.

Hiller, K.H., 1963. Rheological measurements of clay suspensions at high temperatures and pressures. J. Pet. Technol. 17, 779–789.

Hilscher, L.W., Clements, R., 1982. High temperature drilling fluid for geothermal and deep sensitive formations. SPE 10737 paper presented at the California Regional Meeting of the SPE, San Fransisco, CA, March 24 – 26.

Jones, M.N., Bryan, N.D., 1998. Colloidal properties of humic substances. Adv. Colloid Interface Sci. 78, 1–48.

Kelessidis, V.C., Maglione, 2006. Modeling rheological behavior of bentonite suspensions as Casson and Robertson–Stiff fluids using Newtonian and true shear rates in Couette viscometry. Powder Technol. 168, 137–147.

Kelessidis, V.C., Mihalakis, A., Tsamantaki, C., 2005. Rheology and rheological parameter determination of bentonite–water and bentonite–lignite–water mixtures at low and high temperatures. Proceedings of the 7th World Congress of Chem. Engr., Glasgow, 11–13 July.

Kelessidis, V.C., Maglione, R., Tsamantaki, C., Aspirtakis, Y., 2006. Optimal determination of rheological parameters for Herschel–Bulkley drilling fluids and impact on pressure drop, velocity profiles and penetration rates during drilling. J. Pet. Sci. Eng. 53, 203–224.

Kelessidis, V.C., Tsamantaki, C., Mihalakis, A., Christidis, G., Makri, P., Papanicolaou, C., Foscolos, A. in press. Greek lignites as additives for controlling filtration properties of water–bentonite suspensions at high temperatures. Fuel.

Koukouzas, C., Foscolos, A.E., Kotis, T., 1997. Research and exploration of coal in Greece: a view to the future. Energy Sources 19, 335–347.

Kretzschmar, R., Hesterberg, D., Sticher, H., 1997. Effects of adsorbed humic acids on surface charge and flocculation of kaolinite. Soil Sci. Soc. Am. J. 61, 101–108.

Liu, A., Gonzalez, R.D., 1999. Adsorption/desorption in a system consisting of humic acid, heavy metal and clay minerals. J. Colloid Interface Sci. 82, 43–92.

Luckham, P.F., Rossi, S., 1999. The colloidal and rheological properties of bentonite suspensions. Adv. Colloid Interface Sci. 82, 43–92.

Maglione, R., Robotti, G., Romagnoli, R., 2000. In-situ rheological characterization of drilling mud. SPE J. 5 (4), 377–386.

Nyland, T., Azar, J.J., Becker, T.E., Lummus, J.L., 1988. Additive effectiveness and contaminant influence control on fluid loss control of water-based muds. SPE Drill. Eng. 6, 195–203.

Oochs, M., Cosovic, B., Stumm, W., 1994. Coordinative and hydrophobic interaction of humic substances with hydrophilic $Al_2O_3$ and hydrophobic mercury surfaces. Geochim. Cosmochim. Acta 58, 639–650.

Oort, E., Bland, R.G., Howard, S.K., Wiersma, R.J., Roberson, L., 1997. Improving HPHT stability of water based drilling fluids. SPE 37605 SPE/IADC Drilling Conf., Amsterdam, NL, 4–6 March.

Papanicolaou, C., Kotis, T., Foscolos, A., Goodarzi, F., 2004. Coals of Greece: a review of properties, uses and future perspectives. Int. J. Coal Geol. 58, 47–69.

Patel, B.B., 1995. Blended drilling fluid thinner. US Patent 5.399.548.

Rabaioli, M.R., Miano, F., Lockhart, T.P., Burrafato, G., 1993. Physical/chemical studies on the surface interactions of bentonite with polymeric dispersing agents. SPE 25179 Intern. Symposium on Oilfield Chemistry, New Orleans, LA, U.S.A, March 2–6.

Ramos-Tejada, M.M., De Vicente, J., Ontiveros, A., Duran, J.D.G., 2001. Effect of humic acid adsorption on the rheological properties of sodium montmorillonite suspensions. J. Rheol. 45 (5), 1159–1172.

Ramos-Tejada, M.M., Ontiveros, A., del Carmen Plaza, R., Delgado, A.V., Duran, J.D.G., 2003. A rheological approach to the stability of humic acid/clay colloidal suspensions. Rheol. Acta 42, 148–157.

Rebhun, M., de Smedt, F., Rwetabula, J., 1996. Dissolved humic substances for remediation of sites contaminated with organic pollutants. Bridging-desorption model predictions. Water Res. 30, 2027–2038.

Russell, J.A., Patel, B.B., 1987. Drilling fluid. US patent 4.704.214.

Saito, S., Sakuma, S., 2000. Frontier geothermal drilling operations succeed at 500 °C BHST. SPE Drill. Complet. 15, 152–161.

Saito, S., Sakuma, S., Uchida, T., 1998. Drilling procedures, techniques and test results for a 3.7 km deep, 500 °C exploration well, Kakkonda, Japan. Geothermics 27, 573–590.

Santoyo, E., Santoyo-Gutierrez, S., Garcia, A., Espinosa, G., Moya, S.I., 2001. Rheological property measurement of drilling fluids used in geothermal wells. Appl. Therm. Eng. 21, 283–302.

Schulten, H.R., Gleixner, G., 1999. Analytical pyrolysis of humic substances and dissolved organic matter in aquatic systems: structure and origin. Water Res. 33, 2489–2498.

Serpen, U., 2000. Investigation of geothermal drilling muds with high temperature stability. Proceedings World Geothermal Congress, Kyushua-Tohoku, Japan, May 28–June 10.

Sondi, I., Biscan, J., Pravdic, V., 1996. Electrokinetics of pure clay minerals revisited. J. Colloid Interface Sci. 178, 514–522.

Swift, R.S., 1996. Organic matter characterization. In: Sparks, D.L. (Ed.), Methods of Soils Analysis. Soil Sci. Am Book Series, Madison, WI, pp. 1018–1020.

Tarchitzky, J., Chen, Y., 2002. Rheology of Sodium-montmorillonite suspensions: effects of humic substances and pH. Soil Sci. Soc. Am. J. 66, 406–412.

Tombácz, E., Gilde, M., Abraham, I., Szanto, F., 1988. Effect of electrolyte concentration on the interaction of humic acid and humate with montmorillonite. Appl. Clay Sci. 3, 31–52.

Tombácz, E., Filipcseia, G., Szekeres, M., Gingl, Z., 1999. Particle aggregation in complex aquatic systems. Colloids Surf., A Physicochem. Eng. Asp. 151, 233–244.

Tombácz, E., Libor, Z., Illes, E., Majzik, A., Klumpp, E., 2004. The role of reactive surface sites and complexation by humic acids in the interaction of clay mineral and iron oxide particles. Org. Geochem. 35, 257–267.

Visser, S.A., Caillier, M., 1988. Observations on the dispersion and aggregation of clays by humic substances. I. Dispersive effects of humic acids. Geoderma 42, 331–337.

Zamora, M., Power, D., 2002. Making a case for AADE hydraulics and the unified rheological model, paper AADE-02-DFWM-HO-13 presented at the American Association of Drilling Engineers Conference 'Drilling and Completion Fluids and Waste Management', Houston, TX, April 2–3.

Zbik, M., Horn, R.G., 2003. Hydrophobic attraction may contribute to aqueous flocculation of clays. Colloids Surf., A Physicochem. Eng. Asp. 222, 323–328.

Zhang, L.-M., Yin, D-Y., 2002. Preparation of a new lignosulfonate-based thinner: introduction of ferrous ions. Colloids Surf., A Physicochem. Eng. Asp. 210, 13–21.

Zilch, H.E., Otto, M.J., Pye, D.S., 1991. The evolution of geothermal drilling fluid in the imperial valley. SPE 21876 Western Regional Meeting, Long Beach, CA:March 20–22.