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Greek lignites as additives for controlling filtration properties of water–bentonite suspensions at high temperatures

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Abstract

The effectiveness of Greek lignites to control the filtration characteristics of water–bentonite suspensions and to minimize formation damage at high temperatures was studied. Twenty-six lignite samples from various peat/lignite deposits in Greece were used together with a commercial lignite product. The contents of humic and fulvic acids, humins, oxygen, ash and the cation exchange capacity of lignite samples were examined with respect to fluid loss of these suspensions. The results show that most samples provided very good filtration control of the water–bentonite suspensions after exposure to 177 °C with some being superior to the commercial product. Better performance was observed after addition of 3% w/v lignite. Total humic and fulvic acids as percentage of dry lignite matter and the organic matter as lignite percentage showed a weak inverse correlation with the fluid loss volumes.
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Keywords: Drilling mud additive; Filtration control; Humic and fulvic acids

1. Introduction

Drilling fluids are primarily water–bentonite suspensions. They are important for the oil, gas and geothermal drilling industry because they perform many functions like transporting rock cuttings to surface, lubricating the drill bit, applying hydrostatic pressure in the well bore to ensure well safety and minimizing fluid loss across permeable formations by forming a filter cake on the walls of the well bore [1].

When drilling in deep wells for oil, gas or geothermal reservoirs, high temperatures are usually encountered which adversely affect the performance of drilling fluids. In particular, bentonite gels develop which result in loss of filtration control causing formation damage which can

be detrimental not only to the drilling activity but also to later production [2,3] and cause deterioration of the rheological properties of drilling fluids [1,4–8]. At extreme temperatures, special formulations and systems must be used [9–11]. To overcome these problems, organic additives or synthetic polymers have been developed, often called thinners, which stabilize water–bentonite suspensions [1,12,13]. Many of these additives, however, degrade also at high temperatures. Therefore, there is always need for materials which can stabilize water–bentonite suspensions at high temperatures.

Lignite, and particularly an oxidised variety called leonardite, has been used successfully as a thinner for temperatures in excess of 180 °C [1,14–17]. Complexes of lignite and lignosulfonates with specific metals, particularly with Cr^{3+} and Cr^{6+}, have been used as additives for fluid loss control and lignite at 2% and 4% w/w proved to form suspensions with higher thermal stability than lignosulfonate [1,6,18,19]. However complexes with Cr^{6+}

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have serious environmental implications, because Cr^{6+} is carcinogenic.

The effectiveness of the various additives, and in particular lignite with Cr^{3+}, to stabilize filtration control properties of water–bentonite suspensions has been attributed to the ability of the metals to facilitate formation of complexes between lignite and the negatively charged faces of the clay platelets [18–21]. This prohibits face-to-face associations of clay particles which are primarily responsible for the generation of strong gels at alkaline pH [8,22–25]. Reports, however, to explain the effectiveness of pure lignite as additive in water–bentonite suspensions at high temperatures are not available.

Humic acids in lignites may be the factors controlling filtration properties of drilling fluids [1,12,17,18,20]. Direct use of small amounts of humic acids in drilling fluids has been also beneficial [26]. Research on the use and interaction of humic acids with bentonite suspensions in wastewater treatment has been carried out in the past, but at low temperatures, covering the full range of pH [27–34]. The results of these works, particularly at alkaline pH, could be used to interpret the interaction of lignite with smectite particles at high temperatures.

Leonardites, usually characterized as humic matter (complex molecules formed by the breakdown of organic matter), have been reported to contain ca. 13% moisture, 72–85% humic acids, 7% fulvic acids, humin and ca. 15% residue, with 28–35% oxygen content [1,14–16,35]. On the other hand it has been reported that Greek leonardite

may contain 50% humic acids [36] while Spanish leonardite may contain 79% humic acids and 38% oxygen content [37].

Lignite is an abundant indigenous resource for Greece which produces inexpensive electric power [38] with 68 coal basins of various sizes [39]. Some of the basins have proven lignite reserves of insufficient quantity to justify exploitation for power generation. Other means of utilization are thus of significant importance in order to fully exploit these resources and some studies had already been conducted to investigate the use of Greek lignite for non-electric uses [38]. This work reports results of such a study, on the suitability and efficiency of Greek lignite to be used as additive in water–bentonite suspensions to control filtration properties at high temperatures.

2. Experimental

The raw materials were Na-activated bentonite and lignite. The bentonite used is a commercial product (Zenith©) from the island of Milos, provided kindly by S&B Industrial Minerals SA. It consists mainly of montmorillonite (90%) with low layer charge (0.42 per half formula unit) and minor calcite and plagioclase. The bentonite was ground so that 90% of the material is finer than 75 μm [40]. The lignite samples come from basins in different areas of Greece. They are coded after the location (Table 1): Thessaly (code TH), Macedonia and Thrace (code MT), Crete (code KΠ), Peloponese (codes

Table 1
Location, lithotypes, moisture and CEC of lignites used in this study

Code name	Origin	Lithotypes	Moisture %	CEC (meq/100 g organic matter)
Γ	M–I SWACO	Commercial lignite product, caustisized lignite	0.7	121.2
TH1	Thessaly	Peat, clay rich	67.1	175.98
TH2	Thessaly	Peaty muck	56.0	216.67
TH3	Thessaly	Matrix lignite, clay rich	63.2	152.17
TH4	Thessaly	Matrix lignite	46.5	159.99
TH5	Thessaly	Matrix lignite	29.7	137.11
TH6	Thessaly	Xylite rich lignite	31.0	128.03
TH7	Thessaly	Xylite rich lignite	37.4	123.69
TH8	Thessaly	Matrix lignite	30.0	124.5
MT1	Macedonia	Peaty lignite	22.3	78.67
MT2	Macedonia	Matrix lignite	34.3	124.18
MT3	Macedonia	Matrix lignite	25.4	57.37
MT4	Thrace	Matrix lignite, clay rich	19.7	100.08
MT5	Thrace	Matrix lignite	20.6	9.23
MT6	Thrace	Matrix lignite, clay rich	19.8	23.19
MT7	Thrace	Matrix lignite, clay rich	18.7	84.2
MT8	Thrace	Matrix lignite	19.2	122.57
ΠΠ1	Peloponese	Matrix lignite	14.5	158.91
ΠΠ2	Peloponese	Matrix lignite	18.3	154.9
ΠΜ1	Peloponese	Matrix lignite	17.4	145.16
Ι1	Epirus	Matrix lignite	18.9	140.04
Ι2	Epirus	Matrix lignite, clay rich	14.1	166.18
ΚΠ1	Crete	Subituminous coal	9.4	90.61
ΚΠ2	Crete	Subituminous coal	5.7	115.20
ΚΠ3	Crete	Subituminous coal, clay rich	4.7	74.95
ΚΠ4	Crete	Matrix lignite, clay rich	4.2	150.41
ΚΠ5	Crete	Subituminous coal (mixture of ΚΠ1 and ΚΠ2 at a ratio 1:2)	6.9	116.69

ΠΜ and ΠΠ) and Epirus (code I). Shown also in Table 1 are the cation exchange capacity (CEC), determined using a Kjeldahl microsteam apparatus after saturation with ammonium acetate [41], the moisture of the lignites, determined after heating at 105 °C. The ash content was determined after heating at 855 °C, which is a domestic standard specified by Public Power Corporation because of the low rank of Greek lignites. The humic and fulvic acids and humin contents of the lignites were determined according to Swift [42]. C, H, N, O and S were determined according to ASTM D3176-89 [43]. The O_2 content is determined by difference and despite the inherent errors in the approach, it is normally considered adequate [44,45].

The base fluid was made of deionized water and bentonite at a concentration of 6.42% w/w [40] (formula A). To this suspension, lignite was added at concentrations of 0.5% and 3% w/v. The samples with the base suspension (A) containing lignite (*i*) were coded as $A + i$. The performance of the Greek lignites as additives in high temperature drilling fluids was controlled using a commercial lignite additive, which was coded Γ. This material was kindly supplied by MI-SWACO (Caustilig®) and according to the supplier, it is caustisized lignite.

Bentonite and commercial lignite were used as received. The Greek lignite samples were treated before use. Pretreatment involved drying at 105 °C, breaking up the lignite particles in a ball mill to a size of less than 1 mm, followed by grinding in a roll mill so as to pass through a 75 μm sieve. This was followed by treatment with 1 M NaOH (caustisization) which is essential in order to increase the solubility of lignite in the fluid and to make the pH of the drilling fluid alkaline [14,16,17]. The caustisized lignites were dried at 70 °C for two days and were ground further to a particle size less than 75 μm, comparable to the size of bentonite particles.

Preparation of suspensions followed API 13A [40]. Deionized water (500 ml) were mixed in a special mixing cup with 32.1 g of bentonite for the base fluid and the necessary amount of lignite for the lignite samples. The pH values of the suspensions were measured by pH-meter. After mixing, the suspensions were left to age in a sealed container for 16 h at room temperature (hydrated samples) [46] and in an aging cell, pressurized at 7 bar, in an oven at 177 °C for 16 h (thermally aged samples) [1,3,4,6]. Static thermal aging simulates the environment which is encountered by the drilling fluid when left static for long periods in high temperature wells and represents the most severe high temperature testing.

Filtration properties of the suspensions were measured in a low pressure–low temperature (LPLT) API filter press [40]. In the test, a volume of water–bentonite suspension is loaded on the press equipped with a filter paper and a differential pressure of 6.9 bar (100 psi) is applied. A thin, low permeability filter cake is formed on the filter paper resembling the filter cake created during drilling minimizing the amount of filtrate exiting the press. The filtrate collected

over 30 min (fluid loss), expressed in (ml) should not exceed 15 ml [40].

3. Results and discussion

The contents of ash, humic and fulvic acids and humins are given in Table 2. The ash content and the total organic matter content (wt% dry lignite) and the cation exchange capacity (CEC) of lignite (meq/100 g of organic matter) are shown in Fig. 1. The results show that peaty lignites or low rank lignites such as the lignites from Thessaly (code TH), lignites MT2 and MT8, I1 and I2, ΚΠ4, as well as ΠΜ1, ΠΠ1 and ΠΠ2 have higher cation exchange capacity than the commercial one. The sample with the least amount of ash is TH7 containing less amount of ash than the commercial sample.

Fig. 2 depicts humins, humic and fulvic acids and oxygen content as percent of dry lignite. Commercial lignite has less humins and more humic and fulvic acids while oxygen is around 30%. The Greek lignites with comparable to the commercial product properties, on a dry basis, are MT3 and TH4, with over 50% and 45% of humic and fulvic acids, respectively, and similar ash content to the commercial product.

The results of fluid loss of the various water–bentonite–lignite suspensions containing 0.5% lignite are shown in Fig. 3. On the vertical axis the fluid loss value is given while on the horizontal axis the code name of each sample is

Table 2
Organic and inorganic components of lignite samples

| Code name	Ash (% dry lignite)	Humins (% dry lignite)	Humic and fulvic acids (% dry lignite)
Γ	32.78	8.69	58.53
TH1	49.54	17.33	33.13
TH2	59.34	32.67	7.99
TH3	40.20	25.73	34.07
TH4	31.37	23.11	45.52
TH5	40.05	26.20	33.75
TH6	38.53	28.81	32.66
TH7	17.27	48.53	34.74
TH8	30.48	39.70	29.81
MT1	51.95	41.77	6.28
MT2	42.18	25.47	32.35
MT3	32.55	16.40	51.05
MT4	49.84	18.80	31.36
MT5	40.42	19.62	39.95
MT6	52.15	21.19	26.66
MT7	54.04	42.07	3.89
MT8	61.41	35.81	2.78
ΠΠ1	34.67	24.70	40.63
ΠΠ2	33.66	23.09	43.25
ΠΜ1	35.75	23.62	40.63
I1	41.66	27.34	30.99
I2	51.50	20.80	27.70
ΚΠ1	29.37	48.43	22.20
ΚΠ2	50.26	40.10	9.64
ΚΠ3	42.36	19.97	37.67
ΚΠ4	81.85	12.04	6.11
ΚΠ5	42.24	37.65	20.10
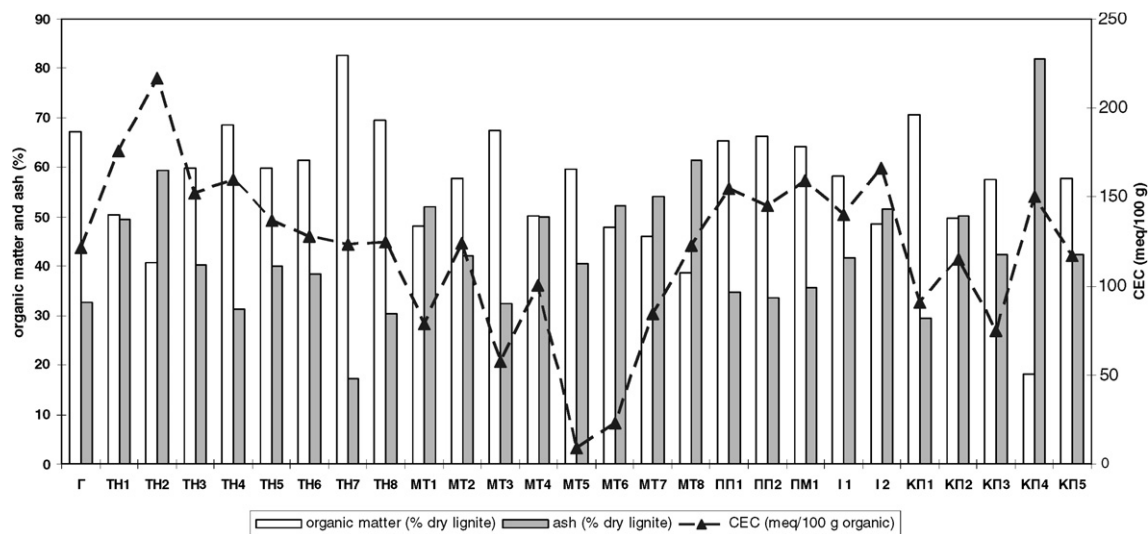
Fig. 1. Ash and organic matter content (wt% of dry lignite) and CEC (meq/100 g of organic matter) of lignite samples.
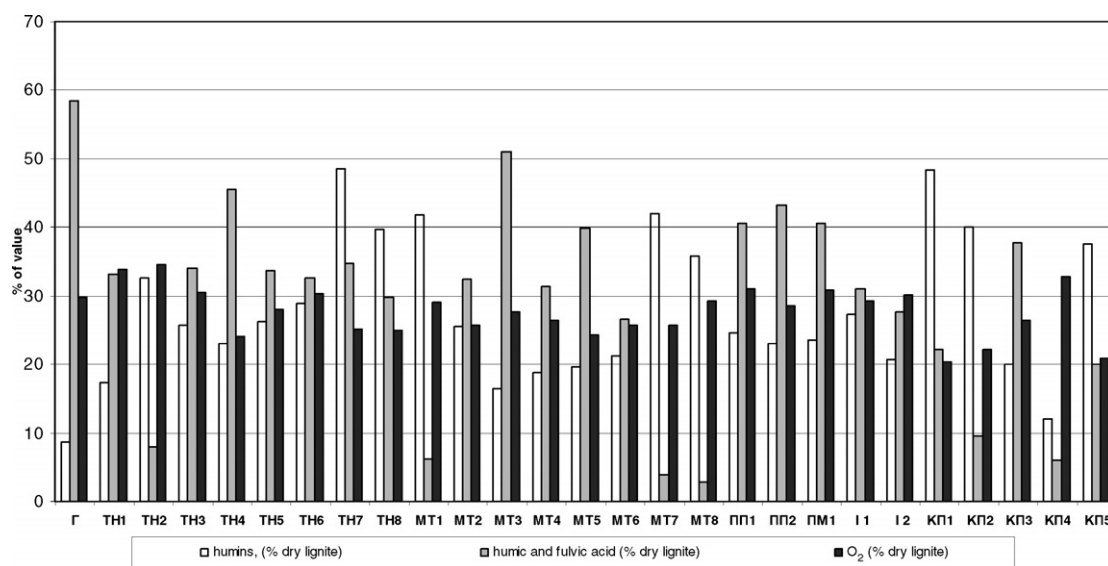

Fig. 2. Composition of the lignites used. Humins, humic and fulvic acids contents and oxygen content are expressed as wt% of dry lignite.
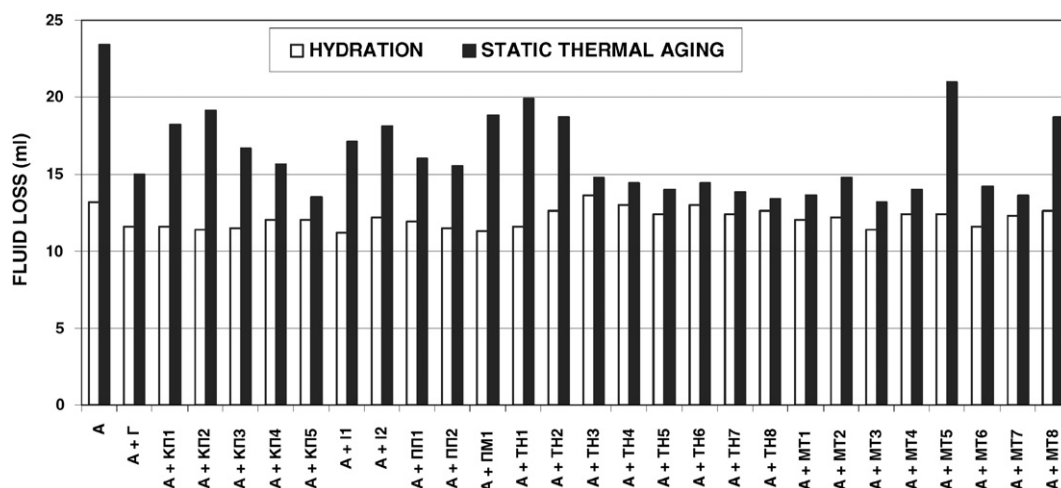

Fig. 3. Fluid loss (ml of fluid) of various bentonite suspensions containing 0.5% lignite and aged by hydration and by static thermal aging at 177 °C for 16 h. 'A' is the base fluid (bentonite suspension).

listed with two bars per sample, one for the hydrated and one for the aged samples. All hydrated samples have performed equally well giving fluid loss values less than 15 ml with the base fluid yielding the maximum value (13.15 ml, the average of two measurements). Half of the Greek lignite samples yielded 11–12 ml fluid loss and the remaining yielded 12–13 ml fluid loss. Thermal aging affects adversely the performance of the base sample fluid yielding an unacceptably high fluid loss value (Fig. 3). The base fluid yielded a filter cake with a fluid loss of 22.3 ml (average of two measurements). Addition of 0.5% lignite improved the performance of the samples and the suspension with the commercial lignite yielded a 15 ml fluid loss. Thirteen of the suspensions containing Greek lignites gave fluid loss values less than 15 ml. Twelve samples yielded fluid loss values between 15–20 ml, and only one sample (MT5) yielded fluid loss greater than 20 ml, still lower than the base sample. Best performance has been observed for samples MT3 (13.2 ml), TH8 (13.4 ml) and KΠ5 (13.5 ml).

The results for fluid loss after addition of 3% lignite are shown in Fig. 4. The fluid loss for the hydrated samples with 3% lignite is considerably lower compared to hydrated suspensions with addition of 0.5% lignite. It varies between 5 ml and 10 ml. Commercial lignite develops the lowest fluid loss (5 ml). The influence of addition of 3% lignite is greater for suspensions subjected to thermal aging in terms of the reduction in the fluid loss values. Twenty-one thermally aged samples yielded fluid loss less than 15 ml whereas KΠ4, TH1, TH2, MT5 and MT8 yielded fluid loss 15–18 ml. Hence, with addition of 3% lignite, most bentonite suspensions meet API specifications for fluid loss. The commercial lignite additive also yielded a low filtrate loss (13.4 ml) and eighteen lignites yielded fluid loss volumes less than the commercial sample. Best Greek lignites were samples TH4 (8.8 ml), TH7 (9.6 ml) and KΠ5 (10.5 ml).

Thermal aging is of particular interest because it simulates the wellbore environment. Furthermore, addition of 3% lignite yielded the best results. Hence, the improvement in the performance of the different suspensions has been calculated in comparison with the performance of the base fluid after thermal aging and addition of 3% lignite. The fluid loss of the base fluid after thermal aging has to be comparable to the value of fresh water–bentonite suspension. Thus, an improvement index, (II), has been employed, defined as follows:

$$II = \frac{\text{base fluid value after thermal aging} - \text{sample fluid value}}{\text{base fluid value after thermal aging}} \times 100 \tag{1}$$

Hence, the ideal (II) would be (23.4–13.2)/23.4 or 44%. An improvement larger than 44% means that the sample fluid performs better than the base fluid at room temperature and yields less fluid loss after thermal aging than the base fluid before thermal aging. The computed (II) for all samples is shown in Fig. 5. There are variations among the performance of different lignites with the improvement index ranging between 26% and 62%, much higher than the ideal of 44%. The commercial sample yields an improvement index of 43%. Highest improvement indices were observed for samples TH4 (62%), TH7 (59%) and KΠ5 (55%).

An attempt was made to correlate the efficiency of the various lignite types to control filtration properties of water–bentonite suspensions after aging at high temperature with their chemical characteristics such as the contents in humic and fulvic acids, humins content, total organic matter, ash and O_2. Fig. 6 shows that there seems to be no direct correlation between fluid loss and chemical composition of lignite. Fluid loss values ranged between 8 ml and 18 ml and total organic matter ranged between 30%
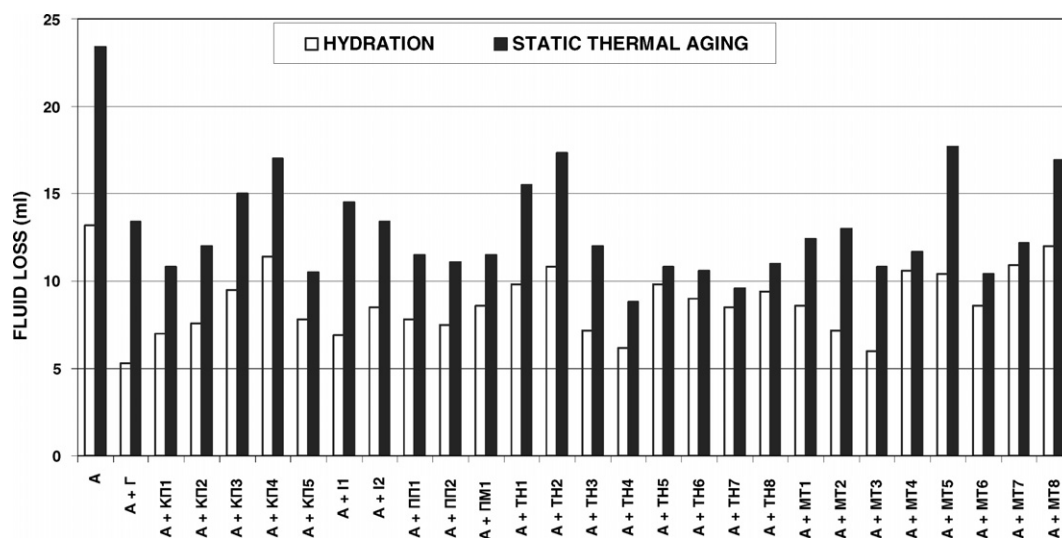

Fig. 4. Fluid loss (ml of fluid) of various bentonite suspensions containing 3.0% lignite and aged by hydration and by static thermal aging at 177 °C for 16 h. 'A' is the base fluid (bentonite suspension).
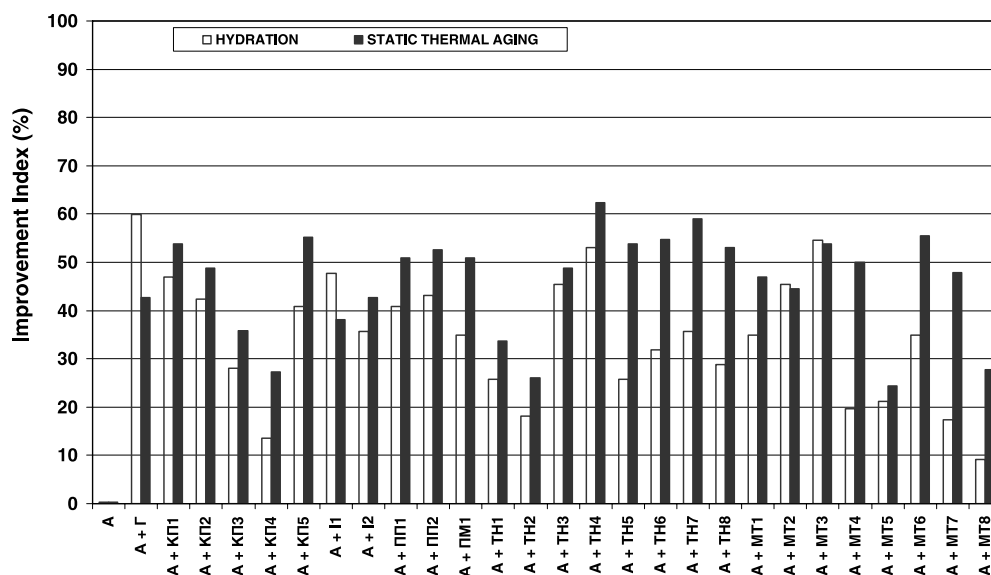
Fig. 5. Improvement index of the bentonite suspensions with respect to base fluid, after addition of 3% lignite and thermal aging at 177 °C for 16 h. 'A' is the base fluid (bentonite suspension).
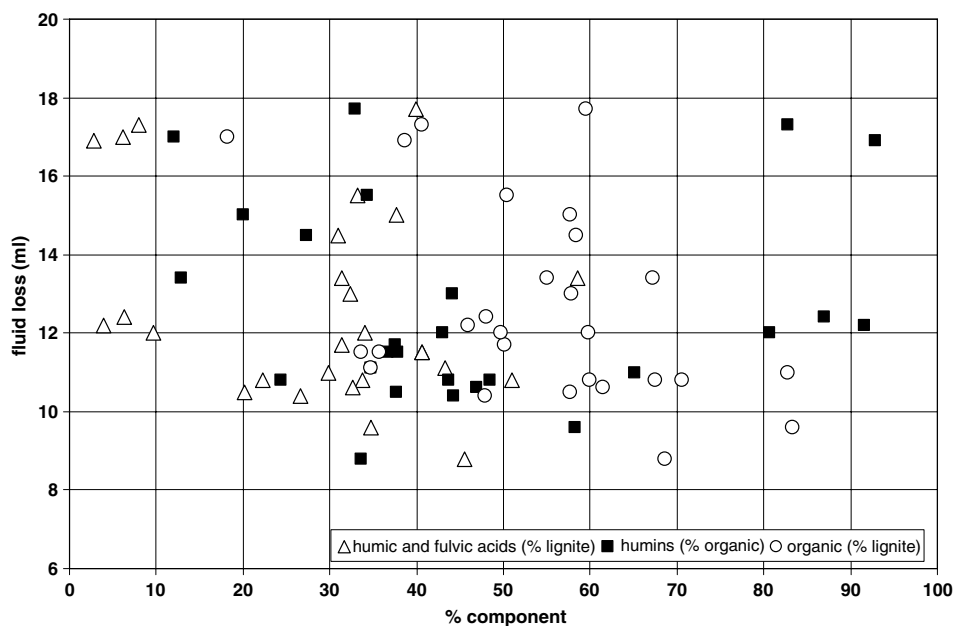

Fig. 6. 30 min fluid loss (ml) from API filter cell of the bentonite–lignite–water suspensions after aging at 177 °C for 16 h as a function of various lignite indices; humic and fulvic acids (wt% of dry lignite), humins (wt% of organic material), and organic material (wt% of dry lignite).

and 90% of dry material. Of this organic substance, humic and fulvic acids constitute 8–90%, while they account for 8–60% of dry lignite. In Fig. 7 there is no obvious direct relationship between fluid loss and the other indices studied, such as the oxygen content, which ranged between 20% and 35% of dry material, the percentage of inorganic material, which ranged between 15% and 60% and the CEC, which ranged between 25 meq/100 g and 220 meq/100 g of organic material. If lignites which yield a fluid loss greater than 15 ml are excluded from the regression, a weak

inverse correlation between fluid loss and humic and fulvic acids content and with total organic matter content is obtained (Fig. 8). Fluid loss is not correlated with the remaining chemical properties of lignites.

Gavrilof et al. [17], studying non-electric uses of lignite found that lignites with high concentration of humic acids, low resin content, low ash content, and low sulphur content yielded the maximum rheological stability and filtration control of water–bentonite suspensions at high temperatures. The concentration of carboxylic and phenolic
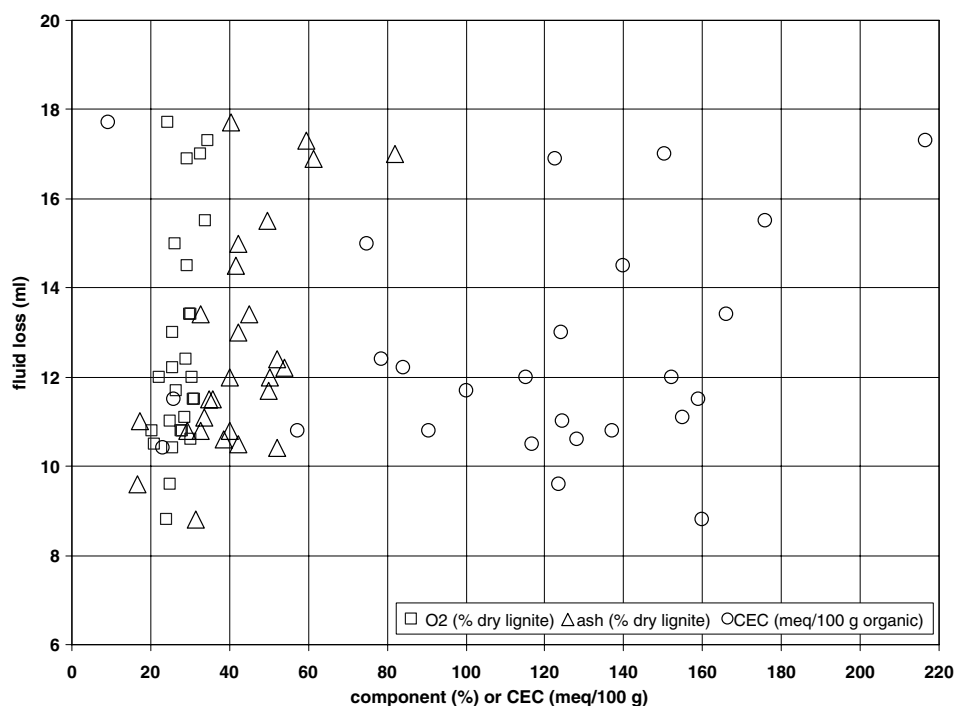
Fig. 7. 30 min fluid loss (ml) from API filter cell of the bentonite–lignite–water suspensions after aging at 177 °C for 16 h as a function of various lignite indices; oxygen (% of dry material), ash (% of total lignite) and CEC (meq/100 g of organic material).
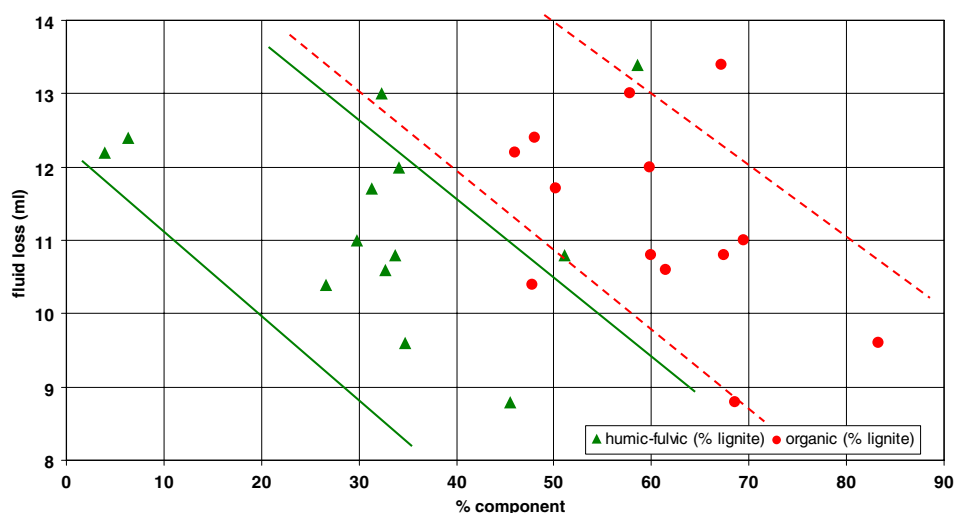

Fig. 8. Fluid loss as a function of humic and fulvic acids (% lignite) and total organic (% lignite) for the samples that gave less than 15 ml fluid loss.

groups was suggested to be the significant parameter affecting the thinning action of lignites because they increased lignite solubility. Humic and fulvic acids are complex, large- to macro-molecules, natural high molecular aromatic acids, consisting mainly of carbon, oxygen, and hydrogen, with over 80% of their oxygen content in the form of carboxylic and phenolic hydroxyls [47] but have poorly defined structures despite the extensive research [48]. Fulvic acids are soluble in water at all pH values and do not adsorb on sodium montmorillonite particles [49], while humic acids are only soluble at pH greater than

2 [48]. Adsorption of humic acids on bentonite is favored at acid conditions and with higher NaCl concentrations [33,34].

It has been reported that adsorbed humic acids molecules on the surfaces of natural clays increase the colloidal stability of clay particles, while removal of humic acids from clay suspensions reduces their colloidal stability [29–32]. The effect of humic acids also depends on bentonite concentration [50,51]. Particle aggregation in montmorillonite–water suspensions was reduced significantly with addition of small amounts of lignite humic acids at pH

from 7 to 8 in the presence of salt [32]. There are reports that the maximum amount of humic acids that can be adsorbed on montmorillonite particles is leveling off in alkaline environment [29,32,48,50]. Filip and Alberts [52] found that up to 90% of humic acids was adsorbed on montmorillonite with preferential adsorption of the aliphatic structures of the humic acids molecules. At all concentrations of humic acids and in both acidic and alkaline environments, adsorption of humic acids has been suggested to occur on the edges of clay particles, as determined from zeta potential measurements [32,50]. This may result in the smearing out of the heterogeneity of the surface charge of the particles providing thus steric and electrostatic stabilization of the suspension by increasing the repulsion among negatively charged particles [32,53].

The mechanism of adsorption of humic substances on clay surfaces could thus be by electrostatic attraction, adsorption via ligand exchange with proton and surface hydroxyl groups, cation binding, water bridging or hydrophobic adsorption [30,33,54]. The electrical charge that the molecules of humic acids bear is then of particular importance. It has been reported to be negative due mainly to ionization of carboxylic and to lesser extent of phenolic groups [33,47,48,50]. Furthermore, the molecules of humic acids become more negatively charged with increasing pH and medium ionic strength [53].

In an alkaline environment, such as the environment of operation of drilling fluids and of this work, it is well known that montmorillonite particles bear negative charge both on their faces and on their edges [8,25,55–59]. The results of the work from previous investigators, referenced above, indicate that the molecules of humic acids bear negative charge, they interact and adsorb onto clay particles, possibly on their edges. If this is the case, a mechanism of binding should be invoked as binding seems to occur between two negatively charged molecules. Filip and Alberts [52] have postulated transformation of appreciable amounts of the adsorbed molecules of humic acids to humins which could not be extracted by alkali from the clay mineral matrix.

Humic acids have also been found to enhance metal adsorption capacity of mineral surfaces [60]. Hence, adsorption of humic acids on clay particles may promote metal adsorption from the suspension onto the mineral surfaces thus aiding metal complexing between the faces of clay particles, which has been claimed to be as one of the main mechanisms for stabilizing water–bentonite suspensions at high temperatures [6].

The results from this work have shown the positive effect of lignite on the stability of water–bentonite suspensions at high temperatures. Addition of various lignite types from different places in Greece in water–bentonite suspensions resulted in retaining their good filtration characteristics even after heating the suspensions to 177 °C for 16 h. It was further shown that weak correlations hold between fluid loss and the organic content of lignites and the humic and fulvic acids content, with higher values of these two parameters yielding, in general, lower fluid loss values. Further work, however, should be carried out to determine not only the components of lignites that control their good functionality as fluid loss additives for filtration control at high temperatures but also the mechanism of binding of the active component of lignite on smectite particles.

4. Summary and conclusions

The ability of various Greek lignites to control the filtration properties of 6.42% bentonite–water suspensions has been investigated after aging the suspensions for 16 h at room temperature (hydration) and for 16 h at 177 °C (thermal aging). A comparison was also made with the performance of a commercial lignite product used as additive. Two concentrations of lignites were studied, at 0.5% w/v and at 3.0% w/v using 26 lignite samples from ten different lignite basins in Greece.

Thermal aging at 177 °C deteriorates significantly the filtration properties of water–bentonite suspensions, giving an unacceptably high value of 22.3 ml, an increase of about 80% from the value of hydrated samples. Full hydration gave acceptable fluid loss volumes, less than the maximum acceptable of 15 ml, for all the samples.

Most of the lignites tested maintained filtration control ability of water–bentonite suspensions after exposure to high temperatures. After addition of 0.5% lignite, half of the lignites tested and the commercial product, yielded fluid loss volumes less than 15 ml after thermal aging, meeting API specifications. The remaining samples yielded fluid loss volumes higher than 15 ml but still less than the value given by the water–bentonite sample. After addition of 3% lignite, 21 of the 26 samples tested yielded fluid loss volumes less than 15 ml, with some of the Greek lignites performing better than the commercial product. The lignite samples TH4, TH7 from the region of Thessaly and KΠ5 from Crete, improved fluid loss by 62%, 59% and 55% respectively, higher than the ideal expected of 44%.

An attempt was made to correlate the performance of the lignite samples with their chemical properties. There is a weak inverse correlation between the fluid loss volume and two lignite chemical properties, the percent organic, and the percent humic and fulvic acids of dry lignite, with less fluid loss at higher concentrations. No distinct correlation was found with the other chemical properties of lignite such as, humins, CEC and O_2 concentration.

Acknowledgements

lignite product Caustilig®. Sample preparation and determination of the particle size distribution were done at the laboratory of ore processing.

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