# Rheological properties of magnesium bentonite and sepiolite suspensions after dynamic ageing at high temperatures.

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ABSTRACT: The rheological properties of three Na-activated, trioctahedral Mg-bentonites (hectorite clay from the CMS Source Clay repository, saponite clay from Spain and stevensite clay from Rhassoul, Morocco) and a sepiolite clay from Greece were examined after dynamic ageing at temperatures up to 230 °C. The 5% w/v suspensions were prepared by dispersing the clay mineral samples in distilled water. The suspensions underwent dynamic, thermal aging for 16 hours before determination of the viscosity, filtration loss, filter cake thickness and pH and the concentration of dissolved $Na^{+}$ and $Mg^{2+}$. Thermal ageing contributed to the dispersion of clay particles, with a direct effect on plastic and apparent viscosity, introducing pseudoplastic behavior. With the exception of the stevensite clay at 230 °C that displayed limited dissolution at 230 °C, the clays were stable at high temperatures. The Na-activation of all clays except for stevensite, was not adversely affected by thermal aging. Thermal aging of stevensite at 230 °C facilitated Na-exchange and yielded suspension with high viscosity and low filtrate loss. Only the suspensions of hectorite and those of stevensite aged at 230 °C met with API specifications. The thermal behavior and rheological properties of the clays might be interpreted with intrinsic properties of the clay minerals, such as layer charge and charge distribution.

KEYWORDS: Mg-bentonite, hectorite, stevensite, saponite, sepiolite, thermal aging, alkali activation, drilling fluids, rheological properties.

## INTRODUCTION

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Drilling fluids are an integral part of the oil and gas extraction process, because they seal and support the walls of the well from the water of the surrounding formations by increasing the hydrostatic pressure inside the well (Mckee & Geehan, 1989). In addition, they serve as coolants and lubricants for the drilling bits, while transporting the fragmented rock to the surface, and they protect the drilling equipment from corrosion (McDonald et al., 2007; Temraz & Hassanien, 2016).

A drilling fluid consists of a fluid phase, in which one or several solid phases are dispersed. The fluid phase can be aqueous (water-based muds or WBMs), oily (oil-based muds or OBMs), gaseous, and emulsions (Vryzas & Kelessidis, 2017; Zhang et al., 2020). The solid phases consist of a series of different materials, which regulate the rheological properties of the suspension, the most important of which are clay mineral nanoparticles (mainly Na-smectite in the form of Na-bentonite, sepiolite and palygorskite) (Güven, 1992; Neaman & Singer, 2000 a,b; Christidis, 2011; Zhang et al., 2020). The main clay material used in drillings is Na-bentonite (Gautam et al., 2018). Smectites, the main mineral of bentonites, are characterized by flaky crystals, with a particle size smaller than 0.5 μm, while carrying a negative electrical charge located in octahedral and/or tetrahedral sites (Odom, 1984; Meunier, 2005). By contrast, palygorskite and sepiolite form fibrous crystals <2μm in size, which are not characterized by significant layer charge (Meunier, 2005). These properties contribute to the formation of stable, non-Newtonian, viscous fluids (Lagaly, 1989; Christidis & Scott, 1996; Christidis, 1998; Neaman & Singer 2000a,b). Additives, namely polymers (xanthan gum, PAC, etc.) (Bavoh et al., 2022), weighting agents (barite, hematite, etc.) (Bageri et al., 2021), and nanoparticles including magnetite, sepiolite, etc. (Gerogiorgis et al., 2015; Al-Malki et al., 2016) are incorporated to the suspensions enhancing their performance.

So far, research studies focus on understanding the rheological properties of Na-bentonites for application in the drilling industry. These studies involve almost exclusively dioctahedral smectites with octahedral charge, mainly montmorillonite (Brandenburg & Lagaly, 1989; Christidis & Scott, 1996; Christidis, 1998; Christidis et al., 2006; Kelesidis et al., 2007; Kelessidis & Maglione, 2008; Vryzas et al., 2017; Vryzas & Kelesidis, 2017) and mixtures of palygorskite or sepiolite with dioctahedral smectite (Chemeda et al., 2014; Al-Malki et al., 2016). In addition, substantial work has been carried out in the last two decades relevant to the rheological behavior of water-based and oil-based sepiolite drilling fluids (, see also Zhang et al., 2020 for a review). Sepiolite enhances the performance of drilling fluids functioning as thixotropic and thickening agents (Alvarez, 1984) and augmenting their gel strength, plastic viscosity, and yield point (Abdo et al., 2016).

Most studies on the rheological properties of water-based and oil-based drilling fluids, prepared with various types of clays, have been performed at room temperature, after aging at room temperature (Brandenburg & Lagaly, 1989; Christidis & Scott, 1996; Christidis, 1998; Neaman & Singer,





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2000b; Christidis et al., 2006; Kelessidis et al., 2007; İşçi & Turutoğlu, 2011; Chemeda et al., 2014; Al-Malki et al., 2016; Zhuang et al., 2018; Echt & Plank, 2019). Studies on the effect of temperature on the rheological properties of clay suspensions at high temperatures and pressures are less common and have been focused mainly on montmorillonite suspensions (Hiller, 1963; Alderman et al., 1988; Briscoe et al., 1994; Santoyo et al., 2001; Kelessidis et al., 2007a, 2007b; Mohammed, 2017; Vryzas et al., 2017), especially Wyoming montmorillonite.

In contrast, studies on the rheological properties of clays with trioctahedral clay minerals, both bentonites and sepiolite, used as drilling fluid additives both at ambient conditions and at elevated temperatures and pressures are limited. Güven et al. (1988) studied the rheological properties of clays rich in saponite, sepiolite, and Wyoming montmorillonite at a temperature range of 149-316 °C and reported high stability and viscosity of the saponite-based fluid when interacting with electrolytes. The rheological behavior of a series of dioctahedral smectites and hectorite at room temperatures were reported by Christidis et al. (2006), while Xiong et al. (2019a,b) observed excellent dispersibility and stability of laponite, the artificial counterpart of hectorite, at high temperatures making it a potential candidate for drilling at high-temperature environments. Laponite is a mixture of hectorite and stevensite with ~25% non-swelling disordered talc (kerolite) layers (Christidis et al., 2018). Laponite was tested also as additive in bentonite suspensions and was reported to be successful for temperature as high as 150 °C (Li et al., 2022). Mixtures of clays containing montmorillonite/saponite or sepiolite/saponite retain and even enhance the advantages of these trioctahedral clay minerals in various applications including drilling fluids (Güven et al., 1987, 1992; Miles, 2011).

Trioctahedral smectites, namely hectorite, stevensite, and saponite, the main constituents of Mg-bentonites, are 2:1 clay minerals, with their octahedral sites occupied by $Mg^{2+}$ cations (Brigatti et al., 2013). Partial substitution of $Li^{+}$ for $Mg^{2+}$ yields the octahedral sheet of hectorite and introduces a negative layer charge (Meunier, 2005). The layer charge of stevensite originates from a small number of vacancies in the octahedral sheet (Brindley, 1984; Christidis & Mitsis, 2006). In the case of saponite, $Si^{4+}$ cations are substituted by $Al^{3+}$ cations in its tetrahedral sheet. Opposite to other smectites, saponite may have positive octahedral charge, due to the replacement of the structural $Mg^{2+}$ cations by $Al^{3+}$ or $Fe^{3+}$, which partially balances the negative tetrahedral charge. (Christidis, 2011; Madejova et al., 2017). Sepiolite is a trioctahedral clay mineral with a fibrous structure (Newman & Brown, 1987), its octahedral sheets being continuous in one dimension forming a ribbon-like structure. The layout of sepiolite tetrahedral sheets consists of inverted tetrahedra in every two or three rows. The above characteristics result in the formation of channels with dimensions 4 Å x 9.5 Å (Brigatti et al., 2013).

In this contribution, new data is provided on the rheological properties of Mg-bentonites with saponite, hectorite, stevensite and sepiolite-rich clay suspensions, and on the ability of these clays to form filter cakes both at ambient tempature and after aging (hot rolling) at elevated temperatures up to 230 °C. The study examines particularly the importance of intrinsic characteristics of the clays on the rheological behavior at these temperatures. Temperatures in excess of 120 °C are encountered in oil drillings below 3000 depth, as well as in geothermal drillings of high enthalpy at shallow depths. Therefore, this work will be useful in predicting the behavior of drilling fluids made by trioctahedral phyllosilicates in high temperature settings, especially considering that the published information on natural Mg-clays is very limited and that the application of synthetic Mg-clay minerals such as laponite is an expensive solution for drilling fluid applications.

## MATERIALS & METHODS

### *Materials*

Four Mg-rich clays were used in this study, 3 Mg-bentonites and one sepiolite sample (Table 1). The bentonites include SHCa-1 from Hector, California, USA (CMS Source Clay Project), a saponite-rich bentonite from Vicalvaro basin, Madrid, Spain and a stevensite-rich bentonite from Jbel Ghassoul, Morocco (Benhammou et al., 2009), known as Rhassoul or Ghassoul clay, supplied by Dr. K. El Ass. The sepiolite sample comes from the rims of magnesite veins in the ophiolite complex of the Euboea Island, Greece and was collected by the senior author.

TABLE 1. Sample notation and origin of clay mineral samples used in this study.

| Samples | Origin |
|---|---|
| SHCa-1 Hectorite | CMS Source clay project |
| Saponite | Spain |
| Stevensite | Morocco |
| Sepiolite | Greece |

### *Characterization methods*

The bulk mineralogy of the samples was determined by X-ray diffraction (XRD), with a Bruker D8 Advance diffractometer equipped with a LynxEye silicon strip detector, using Ni-filtered Cu-Ka radiation (35 kV, 35 mA), 0.298° divergence and anti-scatter slits, a step size of 0.019 °2θ, counting time 1 s per strip step (total time 63.6 s per step), in the 2θ range 4–70°2θ. Data were evaluated with the EVA® software provided by Bruker. Quantitative analysis was performed with the BGMN computer code (*Autoquan*© software package version 2.8) on random powder samples, prepared by grinding with an agate pestle and mortar and mount by careful side loading on Al-holders to avoid preferred orientation.



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Thermogravimetric and Differential Thermogravimetric (TG-DTG) analyses of -2μm fractions of clay the samples were performed with a Perkin Elmer TGA-6 Thermal Analyser, at the Laboratory of Solid Fuels Beneficiation and Technology of the School of Mineral Resources Engineering, Technical University of Crete. The clay fractions were separated according to the Stokes Law after dispersion of bulk samples in distilled water. Analyses were performed an inert atmosphere ($N_2$) in the temperature range 40-900 °C with a heating rate of 10 °C/min.

The major elemental composition of the clay samples was determined by Energy Dispersive X-Ray Fluorescence Spectroscopy (ED-XRF) with a Bruker S2 Ranger ED XRF spectrometer on fusion beads using an 1:1 mixture of Li-tetraborate and Li-metaborate as flux. The Li-content of hectorite and stevensite was determined by Flame Atomic Emission Spectrometry (FAES) with a Perkin Elmer Analyst 100 FAE spectrometer. The SDC-1 standard was used as a Li-rich reference sample. The samples were dissolved with a mixture of HCl, $HNO_3$ and HF acid solutions. The loss on ignition was calculated by heating the samples at 1000 °C. The cation exchange capacity (CEC) of the clays was determined after saturation with 1M ammonium acetate with a Kjeldahl microsteam distillator and titration with 0.05N $H_2SO_4$.

*Rheological properties*

*Viscosity*

The materials were used without any prior purification. They were dried at 105°C, and ground to pass through a 75 μm sieve. The bentonite samples were rendered Na-homoionic by addition of optimum amounts of $Na_2CO_3$ determined from free swelling tests (c.f. Christidis et al*.,* 2006). The suspensions were prepared by the API specifications (API 13A, 2010), except for the concentration of the suspension (5% instead of 6.42 % w/v) by adding the ground clay and the optimum amount of $Na_2CO_3$ in distilled water. The suspensions were stirred for 20 minutes and then were aged for 16 hours at various temperatures (see below). Therefore, the bentonites used for rheological tests were Na-saturated. Activation was not performed on the sepiolite samples. The properties determined were apparent viscosity (AV) plastic viscosity (PV), yield stress and 10 minutes gel strength. The rheological properties of the samples were determined with a Grace 3500a Couette-type viscometer on clay suspensions in distilled water.

Dynamic thermal aging was performed by transferring the agitated suspensions in in stainless steel autoclaves (FANN instruments). Aging was performed at room temperature (25 °C), 100, 149, 176 and 230 °C. After completion of each thermal ageing cycle, the suspensions were cooled down and stirred for 5 minutes and their pH was recorded. pH acts as a stabilization factor of suspensions. In general, alkaline conditions are in favor of the stabilization, since clay particles acquire negative



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overall charges and repel each other (Tombacz et al., 1990; Tombacz & Szekeres, 2004). At acidic pH values, the protons are adsorbed by the active edges of the clay mineral particles, while their edge charges become initially neutral and then positive (isoelectric point, iep) (van Olphen, 1977). The optimum pH for common drilling fluids ranges between 9-10 (Gamal et al., 2019). The rheological experiments after aging at 100 °C and 149 °C were performed in duplicate to estimate the repeatability of the measurements.

The rheological data were handled by the M3600 software and plotted in shear stress vs shear rate charts (rheograms). The obtained curves corresponded to the Power Law, Herschel & Bulkley and Bingham Plastic rheological models and the curves were fitted to the experimental data using an optimization routine written in Matlab. The Herschel & Bulkley model looks identical to the Power Law model, with the difference of the presence of a yield stress parameter in the former (Cheremisinoff, 1986). Since the rheograms showed the existence of a yield stress, $\tau_0$ parameter was constrained to higher than 0 in the Herschel & Bulkley model and all parameters were allowed to vary in the positive range.

*Filtrate loss*

The filtrate loss determination is a simulation of the fluid loss due to filtering of the drilling fluid through the surrounding drilling wall. A low pressure-low temperature (LPLT) filter press (FANN) was used for the experiment. $CO_2$ was used as the pressure medium and it was set at 6.9 atm (~100 psi). The API specifications set the limit of fluid loss for water-based muds at 15 mL for a 30 min test run (API 13A, 2010). The filtrate loss volume collected during the first 7.5 minutes at 6.9 atm was not taken into account (API 13A, 2010). The expelled leachates were stored for further chemical analysis with Flame Absorption Atomic Spectrometry (FAAS), for their Na- and Mg-contents. The solids of those samples aged at 230 °C were dried at 70 °C and subsequently examined by XRD, to trace possible mineralogical changes during thermal aging, using the same experimental setup described for the original materials.

*Filter cake thickness*.

The thickness of the filter cake was measured with a caliper on the filter paper. In normal drilling operations, the cake also includes aggregated clay particles and other particles (i.e., cuttings, weighting agents ets.) of different sizes, which reduce the permeability of the cake (Kelessidis et al., 2006; van Oort et al., 2016). In such cakes, the migration of the finer clay particles in the remaining of the pores and the saturation of the latter with the drilling fluid provide even better sealing performance.





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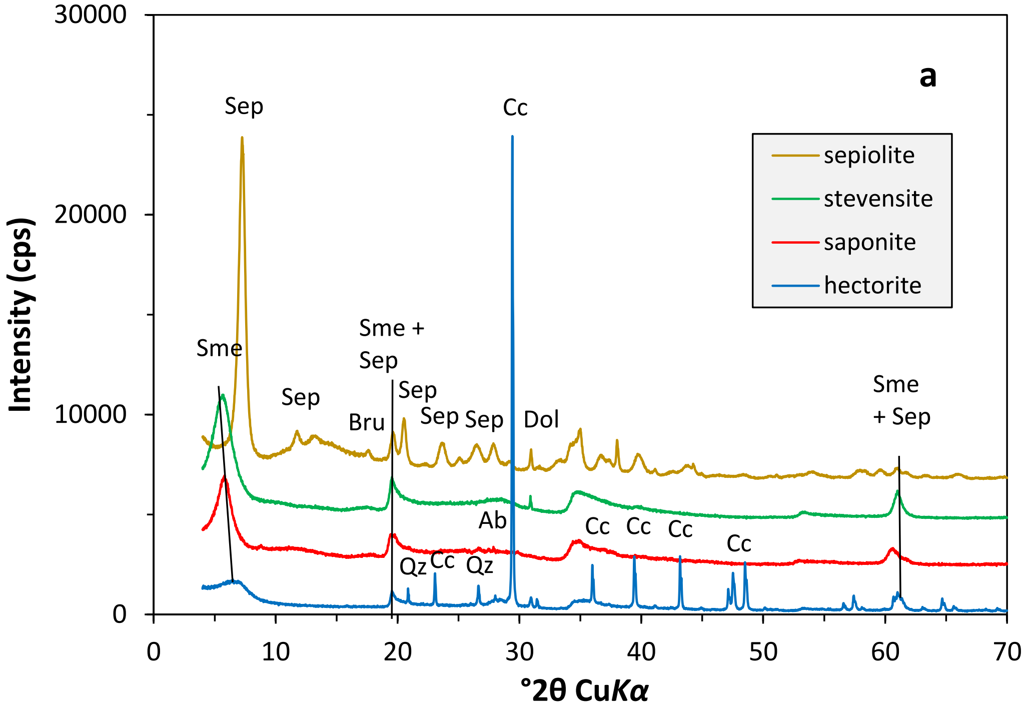
## RESULTS

*Mineralogy of the trioctahedral clays*

The bulk mineralogical composition of the Mg-clays is listed in Table 2. The samples have variable clay mineral contents. The SHCa-1 consists mainly of hectorite and calcite, with minor quartz, dolomite and plagioclase and trace analcime. The stevensite clay consists almost exclusively of smectite (97.1%), with traces of dolomite and K-feldspar. The Spanish saponite sample consists mainly of smectite, with minor illite, quartz, K-feldspar and plagioclase. Finally, the sepiolite sample consists almost exclusively of sepiolite (97.5 wt%) with minor brucite and trace dolomite. All clay minerals display 060 diffraction at 1.525-1.528 Å, confirming the trioctahedral nature of the smectites and the sepiolite.



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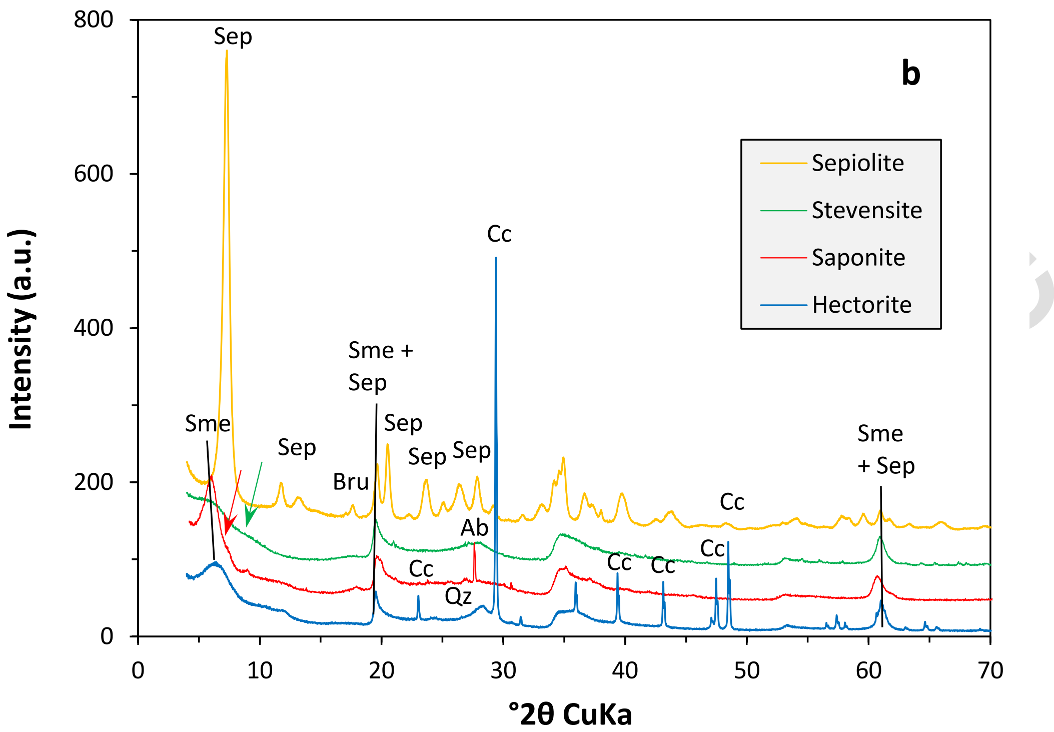


FIG. 1. XRD traces of the trioctahedral clays. a) Original materials, b) materials after thermal aging at 230 °C. The green arrow indicates a ~10.5 Å phase in stevensite and the red arrow indicates a 12.7 Å component in saponite. Key to the symbols: Sme= smectite, Sep= sepiolite, Bru= brucite, Cc= calcite, Dol= dolomite, Qz= quartz, Ab= albite. See text for discussion.

TABLE 2. Mineralogical composition of the clays (wt%). nd= Not detected

| | SHCa-1 | Stevensite | Saponite | Sepiolite |
|---|---|---|---|---|
| Smectite | 48.5 | 97.1 | 85.4 | n.d |
| Sepiolite | n.d | n.d | n.d | 97.5 |
| Quartz | 2.4 | n.d | 1.2 | n.d |
| K-feldspar | n.d | 2.0 | 3.7 | n.d |
| Albite | 2.5 | n.d | 4.4 | n.d |
| Analcime | 0.5 | n.d | n.d | n.d |


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| | | | | |
|---|---|---|---|---|
| Dolomite | 2.3 | 0.9 | n.d | 0.5 |
| Brucite (%) | n.d | n.d | n.d | 2.1 |
| Illite (%) | n.d | n.d | 5.3 | n.d |
| Calcite (%) | 44.0 | n.d | n.d | n.d |

After thermal aging at 230 °C the Mg-clays displayed minor changes. The main modification include the almost total dissolution of dolomite in hectorite, stevensite and sepiolite (Fig. 1a,b). In principle, the Mg-clay minerals were not affected by thermal aging, with the exception of stevensite, in which the 001 diffraction maximum was split in two components one at ~13-14 Å and a minor one at 10-10.5 Å. Also, the Na-exchange was not complete as is indicated by the location of the 001 diffraction maximum, that was centered at 13-14 Å. Saponite displayed a second 001 component in the form of shoulder centered at ~12.8 Å, indicative of partial Na-exchange during aging. The role of Na-exchange on the rheological behavior after thermal aging has been addressed in the discussion section.

*CEC determination.*

Cation exchange capacity of clay minerals is a result of the permanent electric charge, due to isomorphic substitutions in the tetrahedral and octahedral sheets (Johnston & Tombacz, 2002). Additionally, the exposed active edges of the crystals introduce a pH-dependent electric charge, which contributes to the overall charge up to 5% and consequently invigorates CEC (Grim, 1962). Smectites acquire CEC values between 80-150 $cmol_c$/kg of dry clay (Bergaya & Vayer, 1997; Grim, 1968). Stevensite is the only bentonite sample in agreement with the accepted CEC range. Hectorite contains only 48.5% smectite, which explains the reduced cation exchange capacity. Contrary to the expectations, saponite acquires the lowest CEC, even though it contains 85.4% smectite. Sepiolites present lower CEC than bentonites as expected.

*Chemical composition of the trioctahedral clays*

The chemical composition of the studied clays is listed in Table 3 and is in accord with the abundance of trioctahedral phyllosilicates. The MgO is the most abundant constituent after $SiO_2$ in all samples except for hectorite. The hectorite has a high CaO content and LOI and lower $SiO_2$ and MgO contents compared to the remaining samples, due to the presence of abundant calcite and the lower Mg-smectite content. Minor $Li_2O$ is present in hectorite and trace $Li_2O$ (380 ppm) is present in stevensite. The presence of Li is associated with octahedral substitutions of Li for Mg and its presence in the stevensite, indicates the existence of trace hectorite layers in the sample. The saponite is richer in $Al_2O_3$ and $K_2O$ than its counterparts, in accordance with the tetrahedral Al in the mineral and the



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presence of illite and plagioclase impurities. The saponite also has a higher $Fe_2O_3$ content linked with octahedral substitutions. Finally, the sepiolite contains small amounts of NiO in accordance with the origin of the material in ophiolite rocks.

TABLE 3. Chemical composition and cation exchange capacity (CEC) of the studied clays. LOI: Loss on ignition. bdl: Below detection limit

| Elements (wt%) | Hectorite | Saponite | Stevensite | Sepiolite |
|---|---|---|---|---|
| $SiO_2$ | 34.43 | 48.63 | 48.83 | 53.16 |
| $TiO_2$ | 0.03 | 0.28 | 0.13 | bdl |
| $Al_2O_3$ | 1.21 | 8.51 | 2.34 | 0.63 |
| $Fe_2O_3$ | 0.33 | 3.30 | 1.05 | 0.12 |
| MnO | 0.01 | 0.10 | 0.01 | bdl |
| MgO | 15.42 | 24.52 | 27.48 | 26.55 |
| CaO | 23.08 | 1.30 | 1.41 | 0.96 |
| $Na_2O$ | 1.93 | 1.03 | 1.32 | 1.19 |
| $K_2O$ | 0.06 | 1.07 | 0.52 | bdl |
| $Li_2O$ | 0.62 | bdl | 0.04 | bdl |
| P2O3 | 0.54 | 0.02 | 0.20 | bdl |
| NiO | bdl | bdl | bdl | 0.34 |
| LOI | 22.22 | 10.9 | 15.91 | 17.18 |
| Total | 99.88 | 99.65 | 99.25 | 100.12 |
| CEC ($cmol_c$/kg) | 51.5 | 86.2 | 48.6 | 33 |

*TGA/DTGA analysis*

The TGA/DTGA tests provide information about the dehydration and dehydroxylation temperatures of clay minerals (Sainz-Diaz et al., 2001). Trioctahedral smectites dehydroxylate at higher temperatures (~800 °C) compared to their dioctahedral counterparts (<700 °C) (Wolters & Emmerich, 2007). The TG and DTG curves of the <2µm clay fractions are shown in Figure 2. All samples show a main weight loss event due to removal of adsorbed water between 100 and 150 °C (Fig. 2a,b). Stevensite expels the crystalline water in four distinct stages, at ~320, 400-500, 600 and 800 °C (Fig. 2b). The main dehydroxylation event is observed at 800 °C. Hectorite also displays 3 water loss events associated with dehydroxylation, at ~660, ~760 and ~835 °C in accordance with Guggenheim & Koster van Groos (2001). The latter thermal event might receive contribution from trace fine-grained calcite,





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that might also participate in the clay fraction. Considering that the weight loss of hectorite at ~835 °C is due to decomposition of calcite is ~0.20%, it follows that the calcite content in the clay fraction would be ~0.45%. The saponite sample shows two endothermic events a minor one at 500 °C and a major one at >800 °C (Fig. 2b). The event at 500 °C is attributed to the presence - in minor concentration - of illite (Table 2) and possibly to minor stevensite layers that might be present in the sample. The sepiolite sample displays five endothermic events in addition to the low temperature one (at ~100 °C), namely at ~310 °C, ~490 and 550 °C (doublet), 650 °C and 800 °C. The event at 490 °C is associated with the dehydroxylation of minor brucite and that at 650 °C to minor dolomite (Fig. 1, Table 2). Finally, the events at 310, 550 and 800 °C are due to gradual dehydroxylation of sepiolite, with the event at 800 °C receiving contribution from decarbonation of the $CaCO_3$ component of dolomite (Fig. 1, Table 2). Thermal analysis results show that the maximum aging temperature of the fluids is considerably lower than the temperatures of weight loss, due to dehydroxylation of all the trioctahedral smectites and sepiolite. Therefore, the thermal aging is not expected to have caused dehydroxylation of the trioctahedral clay minerals, and any changes in the rheological properties of the suspensions at high temperatures, especially the ones at 230 °C, are not related to structural changes of the clay minerals.

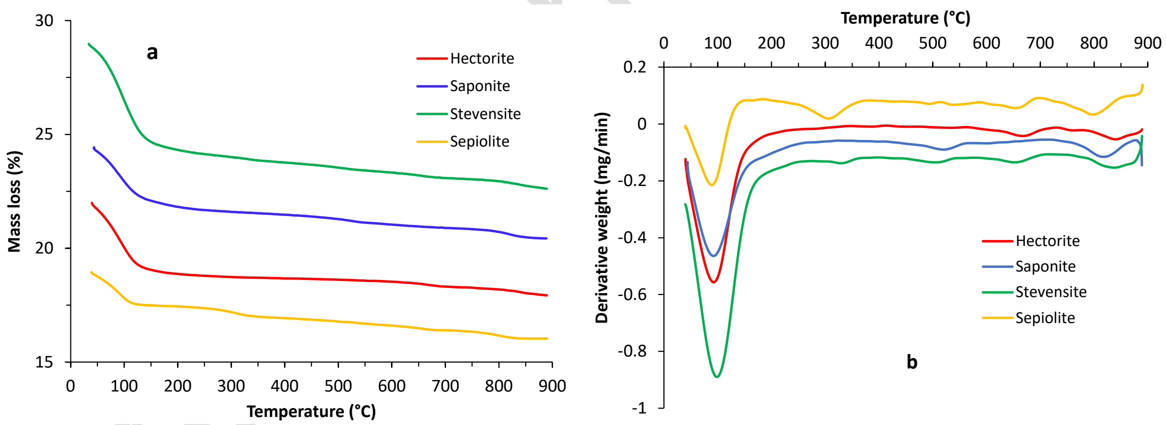


FIG. 2 Thermal analysis of the studied clays. a. TG curves b. DTG curves.

*Rheological properties*

*Rheograms, rheological models and representative rheological parameters.*

Previous work has shown that bentonite-based suspensions display remarkable rheological performance up to 120 °C (250 °F), but at higher temperatures, the addition of rheological additives, namely lignite and xanthan gum has been suggested (Kelessidis et al., 2006).



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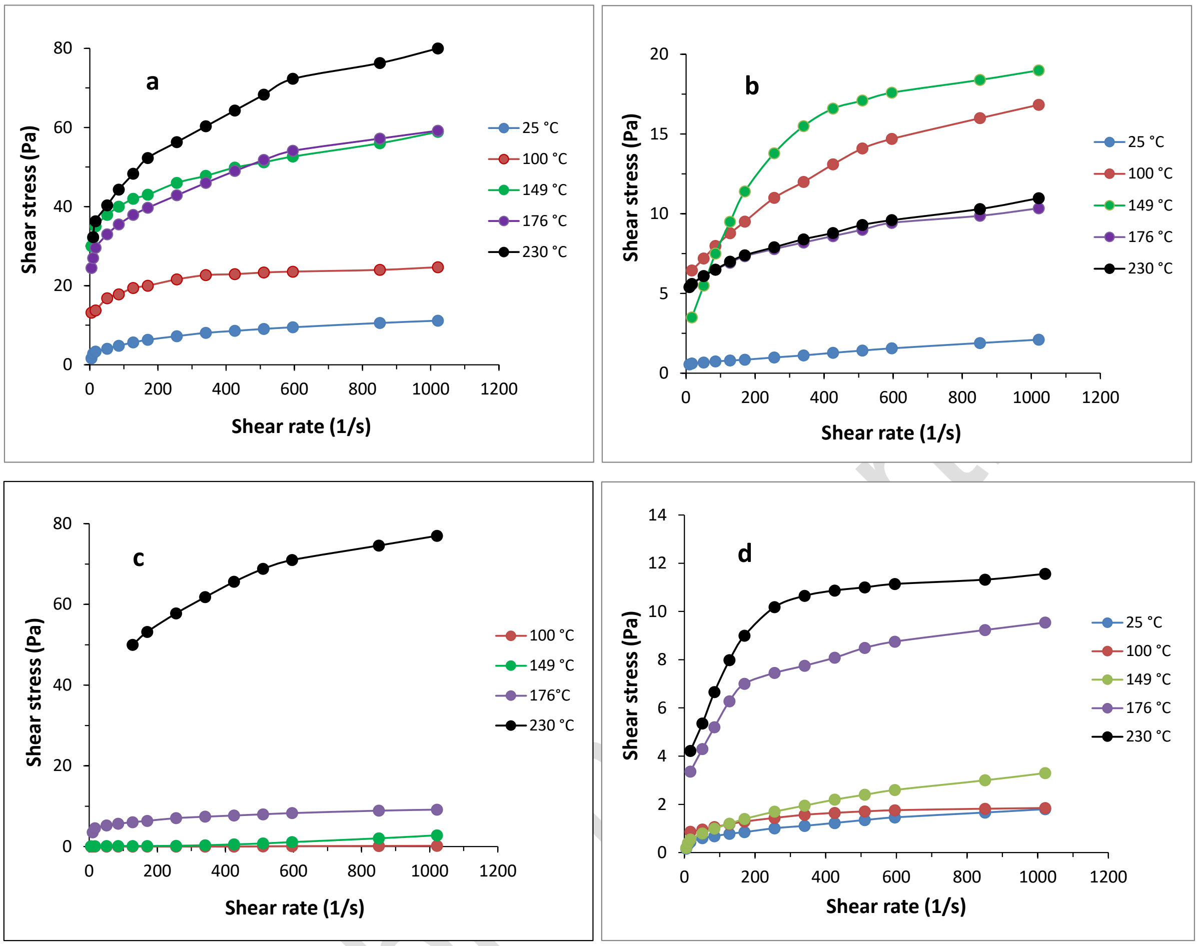


FIG. 3. Rheogramms of the clay suspensions aged at different temperatures. a= hectorite, b= saponite, c= stevensite, d= sepiolite.

The rheograms of the different suspensions are shown in Figure 3, the evolution of viscosity with aging temperature is shown in Figure 4 and the main rheological parameters are summarized in Table 4. Hectorite suspensions became more viscous with increasing temperature (Fig. 3a, 4). The rheological model which describes the flow behavior of the hydrated suspension ( i.e. without thermal ageing) is Power Law. Thermal ageing introduced pseudoplastic flow behaviour, which is described by Herschel & Bulkley model. Power Law and Herschel & Bulkley models express pseudoplastic fluids, since n<1. Gel formation was spontaneous at temperatures higher than 149 °C, which is an indication of extensive delamination of hectorite particles that led to a sharp increase of plastic and apparent viscosity. Gel was completely broken down when shear stress was applied.


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Saponite suspensions presented inferior rheological performance to hectorite (Fig. 3b). Viscosity increased after thermal aging up to 149 °C and decreased at higher temperatures (Table 4), suggesting that the dispersions collapsed at high temperatures. The API standards determine the acceptable apparent viscosity limit at 15 cP i.e. 15 mPa·s (Temraz & Hassanien, 2016), so saponite suspensions at 100 and 149 °C comply with the API specifications, although the suspension concentration was 5% instead of 6.42%. At room temperature saponite dispersion is described by the Bingham Plastic model. After thermal ageing all suspensions are described by the Herschel & Bulkley model (Table 4).

**TABLE 4.** Plastic viscosity (PV), apparent viscosity (AV), and yield point (YP) of the suspensions (PV= $\Phi_{600}$-$\Phi_{300}$, AV=$\Phi_{600}$/2) determined according to API 13A specifications (API, 2010). H&B = Herschel & Bulkley model, BP= Bingham plastic model.

| **Samples** | **Rheological parameters** | **Temperature °C** | | | | |
|---|---|---|---|---|---|---|
| | | **25** | **100** | **149** | **176** | **230** |
| Hectorite | PV (mPa.s) | 10.3 | 19.6 | 49.8 | 50.2 | 69.5 |
| | AV (mPa.s) | 11.4 | 21.0 | 59.7 | 60.8 | 81.4 |
| | Yield Point (Pa) | - | 11.1 | 24.5 | 24.8 | 32.7 |
| | YP/PV | - | 0.57 | 0.49 | 0.49 | 0.47 |
| | Rheological model | - | H&B | H&B | H&B | H&B |
| | $\tau_0$ (Pa) | - | 10.5 | 28.6 | 24.1 | 31.3 |
| | K (Pa.s$^n$) | - | 2.48 | 2.02 | 1.46 | 1.36 |
| | n | - | 0.26 | 0.39 | 0.47 | 0.52 |
| Saponite | PV (mPa.s) | 5.5 | 12.9 | 17.5 | 9.6 | 10.6 |
| | AV (mPa.s) | 6.0 | 15.0 | 19.9 | 7.8 | 9.4 |
| | Yield Point (Pa) | 0.7 | 6.7 | 8.2 | 4.3 | 4.4 |
| | YP/PV | 0.13 | 0.52 | 0.47 | 0.45 | 0.42 |
| | Rheological model | BP | H&B | H&B | H&B | H&B |
| | $\tau_0$ (Pa) | - | 5.3 | 7.5 | 5.1 | 5.2 |
| | K (Pa.s$^n$) | - | 0.25 | 0.20 | 0.15 | 0.11 |
| | n | - | 0.56 | 0.60 | 0.51 | 0.57 |
| Stevensite | PV (mPa.s) | - | - | 3.3 | 9.5 | 72.1 |
| | AV (mPa.s) | - | - | 3.7 | 10.1 | 80.7 |
| | Yield Point (Pa) | - | - | 0.4 | 3.8 | 32.9 |


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| | | | | | | |
|---|---|---|---|---|---|---|
| | YP/PV | - | - | 0.12 | 0.40 | 0.46 |
| | Rheological model | - | - | H&B | H&B | H&B |
| | $\tau_0$ | - | - | 0.3 | 2.20 | 30.1 |
| | K | - | - | 0 | 0.97 | 3.34 |
| | n | - | - | 2.0 | 0.29 | 0.38 |
| Sepiolite | PV (mPa.s) | 1.2 | 2.1 | 3.1 | 8.4 | 11.1 |
| | AV (mPa.s) | 2.1 | 2.4 | 3.7 | 9.5 | 11.9 |
| | Yield Point (Pa) | - | - | - | 4.1 | 5.3 |
| | YP/PV | - | - | - | 0.49 | 0.48 |
| | Rheological model | - | - | - | H&B | H&B |
| | $\tau_0$ | - | - | - | 3.2 | 3.8 |
| | K | - | - | - | 0.44 | 0.81 |
| | n | - | - | - | 0.39 | 0.34 |

The stevensite suspensions were completely inert at temperatures below 176 $^{o}$C, with shear stress values being close to the detection limit of the viscometer (5 dyn/cm$^2$) for the suspensions aged at 25 and 100 $^{o}$C (Fig. 3c, 4). However, the suspensions did not show evidence of collapse. The formation of a suspension with high plastic and apparent viscosity and yield point at 230 $^{o}$C (Fig. 3c, 4 Table 4) was an unexpected result, which suggests possible delamination of stevensite particles and formation of particle networks.

In the sepiolite suspensions, higher temperatures facilitated hydration of particles, leading to augmented rheological behavior (Altun et al., 2010). Indeed, the viscosity increased gradually with the temperature of aging, although the viscosity of the suspensions after aging up to 149 $^{o}$C is very low (Fig. 3c, 4 Table 4). Despite the profound increase of the viscosity, sepiolite does not comply with API specifications, because it formed thin suspensions, which however did not collapse or aggregate. Sepiolite consists of fibrous or particles, whereas smectites in bentonites form mostly flake/platelet-like crystals (Christidis, 2011). The latter introduce larger hydrodynamic drag and thus contribute to the formation of viscous suspensions. The sepiolite displays plastic flow behavior at temperatures higher than 176 $^{o}$C (Fig. 3c, Table 4).





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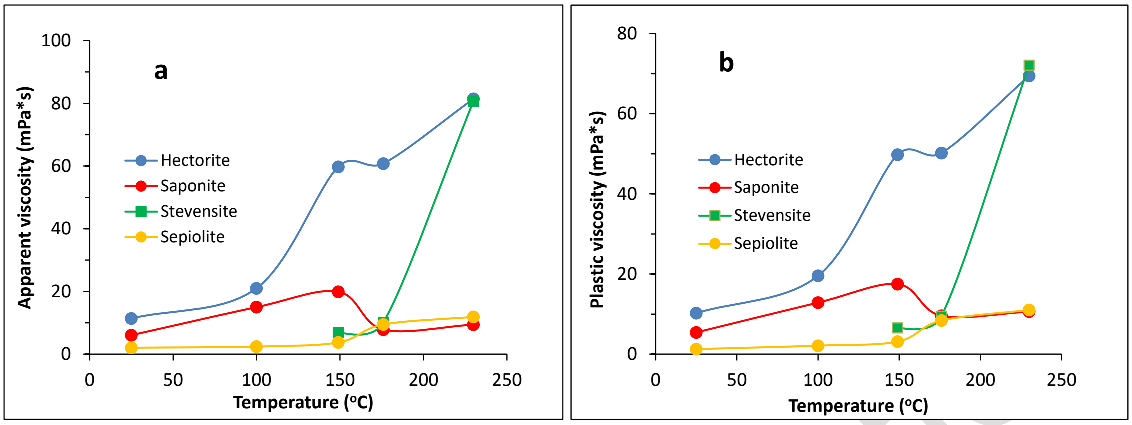


FIG. 4. (a) Apparent viscosity and (b) plastic viscosity of the suspensions as a function of temperature

Except for the viscosity, Table 4 summarizes the yield point (YP) values and YP/PV ratios of the suspensions, as well as the $\tau_0$, K and n values for the Herschel & Bulkley model corresponding to the yield stress, the consistency index and the flow-behavior index of the suspension. These parameters were obtained both from the curve fitting Herschel & Bulkley model and from the logarithmic form of the Herschel & Bulkley equation, namely $\log(t\text{-}t_0) = \log K + n\log(\gamma)$. The YP is affected by the particle interactions via van der Waals attractive forces (Vryzas et al., 2016). The maximum acceptable value for YP is 18 lb/100 $ft^2$ (~8.6 Pa) according to the API 13A (2010). YP/PV ratio expresses the pseudoplastic (shear thinning) behavior of the suspension (Safi et al., 2016) and the maximum acceptable value is 3 (API 13A, 2010). Both of the aforementioned limits apply to bentonite muds. Distinct limits for sepiolite dispersions are not available. The YP/PV ratios of all suspensions conform to the API specifications, although the solid content was 5% instead of 6.42%.

The YP during the experiments vary among materials. In general, the YP of the suspensions increase with temperature, with a more profound effect in the case of hectorite (Fig. 5). A similar trend was observed for dioctahedral Wyoming montmorillonite for aging temperatures up to 80 °C (Vryzas et al., 2017). In fact, gel formation in hectorite suspensions was pronounced at temperatures higher than 149 °C with the yield point exceeding the maximum acceptable limit (i.e. ~8.6 Pa). The same applied to the stevensite suspension aged at 230 °C. The remaining stevensite suspensions yielded low or undetectable yield points. Saponite and sepiolite muds exhibited low yield points and compliance with the API regulations (minimum yield point 1.5 Pa); thus the yield point of these


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suspensions would not undermine their ability to transport the fragmented rock during drilling operations.

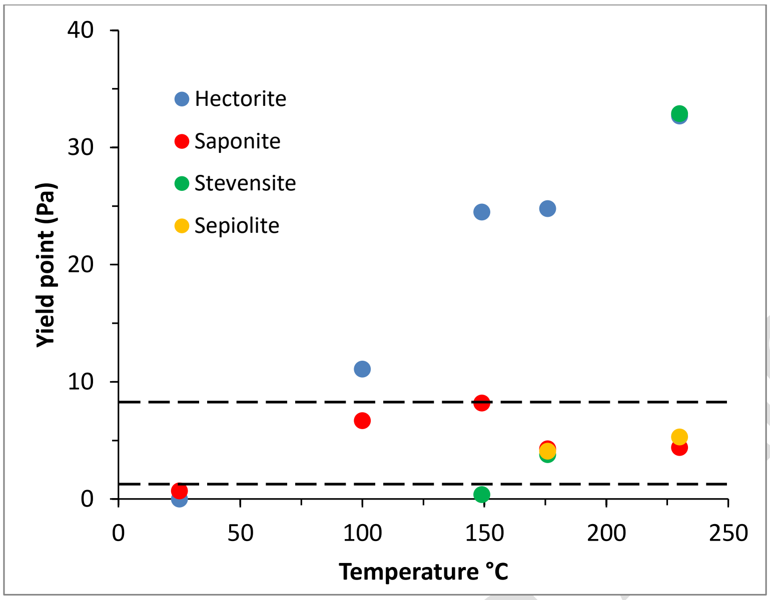


Fig. 5 Yield point of the examined suspensions after aging at different temperatures. The dashed lines indicate the minimum and maximum yield point values (in Pa) accepted by the API13A (2010)

The $\tau_0$, K and n parameters for the suspensions of the different Mg-clays at the various temperatures display certain trends (Table 4). In hectorite the yield stress ($\tau_0$) and flow-behavior index (n) values increase with increasing aging temperature, whereas the consistency index (K) follows the opposite trend. Similar to hectorite, the K parameter of the saponite decreases gradually with increasing aging temperature, whereas the $\tau_0$ and n parameters are maximum after aging at 149 °C, decreasing at higher aging temperatures, similar to the viscosity of the suspensions (Fig. 5). The stevensite suspensions displayed a gradual increase of the $\tau_0$ and K with increasing temperature, whereas n did not display a clear trend. Finally, sepiolite suspensions displayed a gradual increase of the $\tau_0$ and K, and a gradual decrease of n with increasing temperature (Table 4). In conclusion, all clay suspensions displayed an increase of $\tau_0$ with increasing temperature, but sepiolite suspensions displayed opposite trends with respect to consistency index and flow-behavior index trend compared the hectorite and saponite counterparts, at least at high aging temperatures, for which sepiolite data is available. The trends for $\tau_0$ K and n observed for hectorite and saponite suspensions with increasing temperature are in agreement with similar studies with suspensions of bentonites with dioctahedral smectites (Vryzas et al., 2017). In contrast, the trends for $\tau_0$ K and n observed for stevensite suspensions are in general agreement with bentonite suspensions based on dioctahedral smectites, that contained laponite as



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additive (Li et al., 2022). However laponite is not a pure phase but a mixture of 50% hectorite layers with 25% stevensite and 25% kerolite layers (Christidis et al., 2018).

*pH measurements*.

The pH plays a key role in the performance of a multiphase fluid. Acidic conditions are not in favor of a bentonite-based suspension because the negative, overall surface charge of the smectite particles is gradually neutralized and thus the electric double layer (EDL) is compressed (Park & Seo, 2011). This causes flocculation and sedimentation of particles. On the other hand, alkaline conditions contribute to the efficient dispersion of clay particles, since the net surface charge, which consists of the permanent and pH-dependent edge charges, is negative and the EDLs expand and repel each other (Tombacz & Szekeres, 2004). The pH values obtained after aging at different temperatures are listed in Table 5. The pH of suspensions increased with increasing aging temperature in all the trioctahedral clays (Table 5, Fig. 6a). The rheological parameters (PV, AV, YP) are improved at pH values above 10 (Alaskari & Teymoori, 2007), which is also the case for most of the suspensions prepared in this study. In particular the PV displays a well-expressed exponential increase with increasing pH, except for the sepiolite suspension aged at 230 °C (Fig. 6b).



TABLE 5. pH measurements of the suspensions after 16 hours of hydration (25 °C) or thermal ageing.

| Samples | 25 °C | 100 °C | 149 °C | 176 °C | 230 °C |
|---|---|---|---|---|---|
| Hectorite | 7.32 | 10.08 | 10.57 | 11.72 | 12.46 |
| Stevensite | 6.74 | 7.89 | 8.13 | 8.58 | 11.88 |
| Saponite | 7.56 | 7.61 | 9.37 | 9.15 | 9.52 |
| Sepiolite (G) | 6.24 | 8.22 | 8.64 | 9.01 | 11.89 |

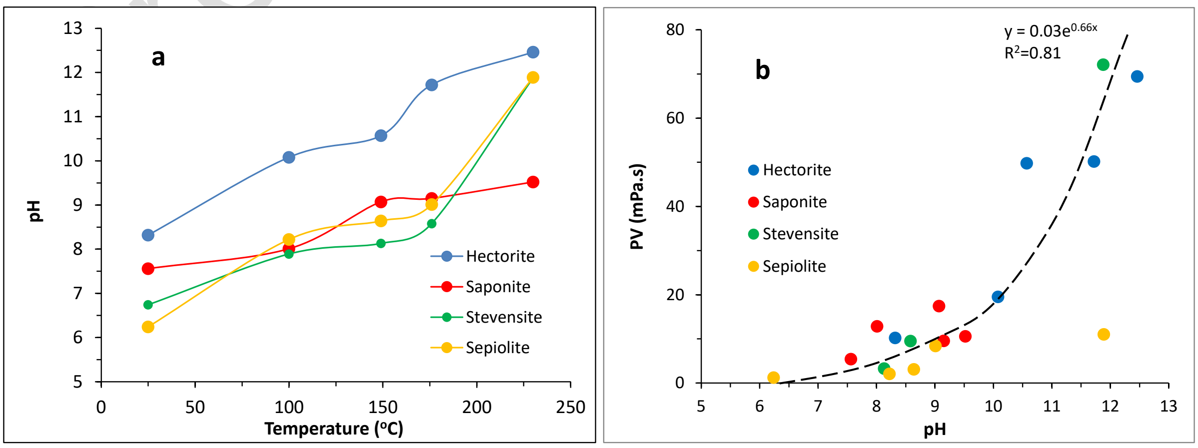




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Fig. 6. a) Evolution of the pH of the suspensions with temperature b) evolution of Plastic Viscosity (PV) with pH.

The hectorite suspensions are typical examples of the influence of alkaline pH on the rheological properties, since the rheological behavior was improved considerably compared to the remaining clay minerals (Fig. 6b). The same applied to the stevensite suspension at 230 °C. Saponite suspensions became more alkaline with increasing temperature, and despite their collapse at 176 °C (sharp decrease of the viscosity in Fig. 6b), the pH continued to increase. The pH of sepiolite suspensions ranged between 6.2 and ~ 9 increasing sharply at 230 °C (Fig. 6a), and the PV increased sharply at 176 °C remaining constant at higher temperatures (Fig. 6b).

*Filtration loss and filter cake thickness.*

The stevensite and sepiolite suspensions did not comply with the maximum acceptable filtration loss of 15 mL, according to the API 13A (2010) regulations for water-based drilling fluids (Fig. 7a). On the other hand, hectorite and saponite muds did not produce large filtrate volumes. In fact, the increase of temperature contributed to the reduction of the filtration loss. Saponite suspensions collapsed at 176 and 230 °C, leading to extensive particle precipitation, which nevertheless did not significantly increase the filtrate loss (Fig. 7a). The remaining filter cakes became thicker with increasing temperature for both saponite and hectorite suspensions. The thicker the filter cake was, the more difficult it was for the fluid to penetrate it.

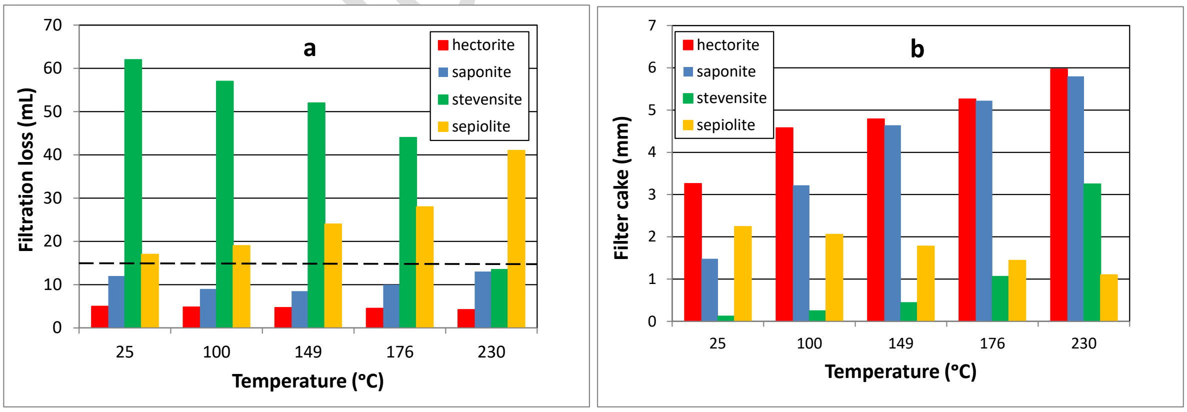


Fig. 7. a) Filtration loss of the suspensions b) and thickness of the filter cakes after aging at different temperatures. The dashed line in 8a indicates the maximum acceptable filtrate loss according to API 13A (2010).

Stevensite suspensions expelled large volumes of fluid, far beyond the accepted limit. However, after a thermal ageing cycle at 230 °C, the dispersion became viscous and the filtration loss complied



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with the API 13A specification, forming a thick filter cake (>3 mm). The sepiolite also displayed high filtration loss at all temperatures, indicating gel structures with open pores. Opposite to the smectite suspensions, the performance of sepiolite became poorer with increasing temperature. The filter cakes of the sepiolite suspensions were thin, acquiring a maximum thickness of 2.25 mm at 25 °C aging temperature (Fig. 7b).

A well-defined overall negative exponential trend holds between the filtrate loss and thickness of the filter cakes (Fig. 8), indicating an association of high filter losses with thin filter cakes, as expected. Maximum filter cake thickness/minimum filtrate loss was observed at higher aging temperatures, with the sepiolite suspensions deviating from the overall trend. In general, a filtrate loss lower than 15 ml was observed in filter cakes thicker than ~3 mm, except for the saponite suspension aged at 25 °C (Fig. 8).

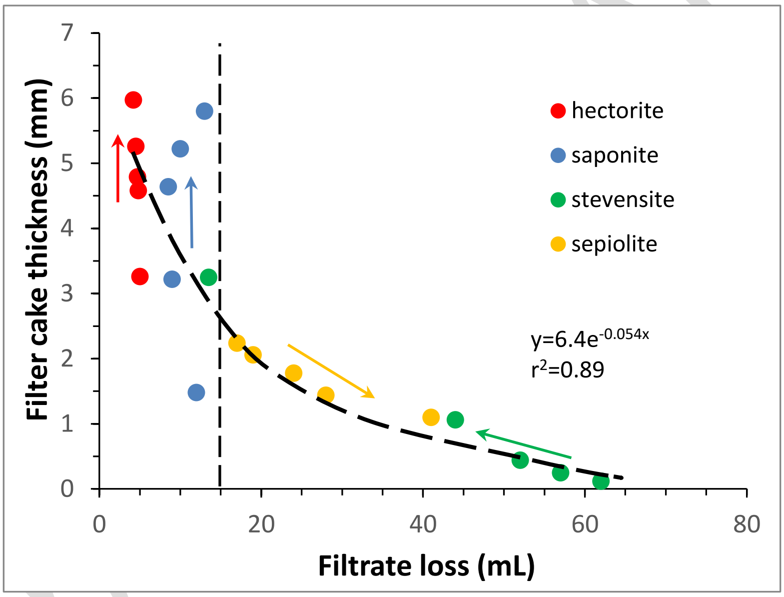


Fig. 8. Filtrate loss vs filter cake thickness of the suspensions aged at different temperatures. The arrow in each clay mineral indicates the direction of increasing aging temperature. The dashed line indicates the maximum acceptable filtrate loss according to API 13A (2010).

*Chemical composition of the filtrates*.

Table 6 lists the concentrations of $Na^+$ and $Mg^{2+}$ cations of the filtrates. The $Na^+$ and $Mg^{2+}$ concentrations were used to assess the extent of cation exchange on bentonites after alkaline activation. In addition, the magnesium content was used to monitor possible decomposition of the smectite and sepiolite particles during thermal aging.

The different bentonites display different trends with respect to the Na-content of the filtrates. The Na-content of the hectorite filtrates increases with increasing temperature reaching a plateau



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above 176 °C, whereas the Na-content in the saponite decreases slightly and in the stevensite filtrates it decreases significantly, especially after aging at 230 °C. The high Na-content of the stevensite suspensions, indicates that aging up to 149 °C does not facilitate Na-exchange, that begins at 176 °C and is more effective at 230 °C. The effective Na-exchange at 230 °C is reflected in the improved rheological properties. On the other hand, the relatively low $Na^+$ content of the hectorite suspensions indicates a successful cation exchange during activation, in accord with the superior rheological properties of the suspensions. Finally, the saponite filtrates also have relatively high sodium contents suggesting an incomplete cation exchange.

Similarly, the Mg-content of the filtrates varies among the different clay suspensions. The hectorite filtrates display a rather constant and high Mg-concentrations up to 176 °C that increases further after thermal aging at 230 °C, although the amount of $Mg^{2+}$ remains essentially constant at ~0.6 meq throughout the whole aging temperature range, because the filtrate volume decreased (Fig. 7a). Ion exchange (i.e. Na for Mg), although it might take place to some extent, is not considered the main driving force for the $Mg^{2+}$ contents in the hectorite filtrates because of the considerably high Mg/Na meq ratios (Table 6). In contrast, the saponite and sepiolite filtrates display low Mg-contents. Finally, the stevensite filtrates have moderate Mg-concentrations that increase after aging at 176 °C and especially at 230 °C. However, the total amount of Mg in meq in the stevensite filtrates tends to decrease with increasing aging temperature because the filtrate volume decreased considerably (Fig. 7a, Table 6). Similar to the hectorite suspensions, ion exchange, is not the main driving force for the $Mg^{2+}$ contents in the stevensite because of the high Mg/Na meq ratios (Table 6). In contrast, the Na for Mg exchange in saponite might be the dominant mechanism controlling the concentrations of these ions in the filtrates, due to the considerably high Na/Mg meq ratios (Table 6).

TABLE 6. Concentration of $Na^+$ and $Mg^{2+}$ cations (ppm) in the filtrates at various aging temperatures. The values in brackets are the amounts of $Na^+$ and $Mg^{2+}$ in meq.

| **Samples** | **$Na^+$** | | | | | **$Mg^{2+}$** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **25°C** | **100°C** | **149°C** | **176°C** | **230°C** | **25°C** | **100°C** | **149°C** | **176°C** | **230°C** |
| **Hectorite** | 183 (0.04) | 254 (0.05) | 365 (0.07) | 504 (0.1) | 532 (0.1) | 1547 (0.64) | 1426 (0.57) | 1614 (0.63) | 1479 (0.56) | 1854 (0.65) |
| **Saponite** | 1809 (0.94) | 1723 (0.90) | 1703 (0.89) | 1706 (0.89) | 1659 (0.87) | 46 (0.05) | 89 (0.07) | 111 (0.08) | 108 (0.09) | 137 (0.15) |
| **Stevensite** | 7044 (19.0) | 7053 (17.5) | 6988 (15.8) | 5322 (10.2) | 1078 (0.63) | 587 (3.04) | 594 (2.82) | 612 (2.65) | 898 (3.23) | 2006 (2.26) |
| **Sepiolite** | - | - | - | - | - | 35 (0.05) | 45 (0.07) | 49 (0.1) | 61 (0.14) | 66 (0.23) |





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The Mg-content displays a positive trend with the pH of the filtrates for the hectorite and the stevesite suspensions (Fig. 9), suggesting a contribution of dissolved Mg on the alkalinity of the suspension. The saponite and sepiolite suspensions do not follow this trend, due to their low Mg-contents. The increase of Mg-concentration in the hectorite and stevensite suspensions with temperature is in accordance with the increase of the pH of filtrates with temperature (Table 5, Fig. 6a).

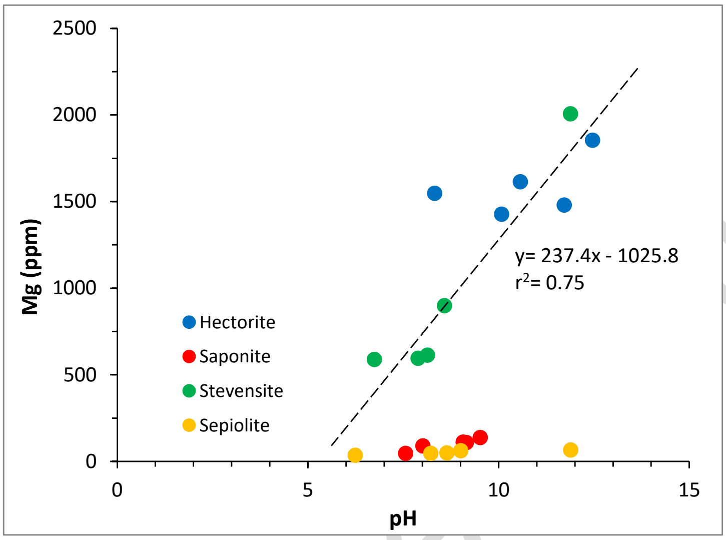


Fig. 9. pH vs Mg content of the suspension filtrates after aging at different temperatures

## DISCUSSION

*Response of the trioctahedral clays to high temperature aging*

The present study showed that the different trioctahedral clay minerals display different rheological properties and that the filtrate compositions can also vary significantly after thermal aging. The $Na^+$- and $Mg^{2+}$-contents of the filtrates are controlled by ion exchange and structural stability of the trioctahedral clay minerals. Considering the Mg-content of the filtrates after thermal aging as a proxy for the stability of the clay minerals, when the Mg-content exceeds the Na-content, sepiolite displayed higher thermal stability than the trioctahedral smectites and saponite had the greater thermal stability among all the trioctahedral smectites (Table 6). On the other hand, hectorite filtrates had high $Mg^{2+}$-contents that tended to be constant up to 176 °C, increasing slightly after aging at 230°C (Table 6). The high $Mg^{2+}$-contents, even at ambient temperature, suggests that the Mg-content of the filtrates might not result mainly by dissolution of smectite, but rather from dissolution of other Mg-bearing phases, such as dolomite, or from dissolution of soluble Mg-salts. Indeed, the XRD results showed that dolomite dissolved after thermal aging of the hectorite. Therefore, hectorite displayed very good thermal stability at high temperatures, that is comparable to that of saponite.



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The low Mg-content of the saponite filtrates might be also attributed, at least partially, to Na-for Mg exchange. In any case, saponite displayed inferior rheological properties at high temperatures compared to the remaining trioctahedral smectites, and its suspensions collapsed at temperatures higher than 149 °C (Table 4, Fig. 5). In contrast, both hectorite and stevensite suspensions, with higher Mg-contents, yielded viscous suspensions at high temperatures. The Na- and Mg-content of the stevensite filtrates might also indicate limited Na- for Mg-exchange as noted before. However, the existence of octahedral vacancies in the stevensite structure, due to the lack of octahedral Mg, suggests that Mg was not exchangeable and that the $Mg^{2+}$ in the filtrates was probably due to modifications of the stevensite structure, except for the dissolution of dolomite. The appearance of a diffraction maximum at 10-11 Å (Fig. 1b), that might be attributed to kerolite layers is in accordance with such a modification. This complex behavior suggests that rheological properties at high temperatures might not be associated only with the stability of the crystal structure and particle morphology of the different trioctahedral clay minerals. Two additional parameters are considered further: the role of Na-exchange (Na-activation) and the intrinsic properties of clay mineral particles, related to crystal structure.

Sodium exchange was relatively effective in hectorite, the filtrates of which showed low Na-contents that slightly increased with increasing aging temperature. This is indicated also in the $d_{001}$ of hectorite after thermal aging (13-14 Å, Fig. 1b). The presence of Mg-ions in the suspension, due to dissolution of dolomite, explains the incomplete Na-exchange in hectorite. A possible negative influence of temperature on Na- for Ca/Mg-exchange (e.g. Deist & Talibudeen, 1967) is not considered important because the exchange was not complete at room temperature in all filtrates, except for those of hectorite; instead, it was effective in stevensite at 230 °C (Table 6). In addition, the saponite filtrates had high Na-contents at all aging temperatures, with a tendency to decrease slightly with increasing temperature, especially at 230 °C, and low Mg-contents. The lack of a particular trend in the Na-content of filtrates with temperature suggests that Na-exchange might be controlled by the intrinsic properties of the individual smectites rather than the temperature. The intrinsic properties considered in this study are layer charge and charge localization.

Layer charge affects ion exchange both in univalent and bivalent cations (Maes & Cremers, 1977, 1978; Shainberg et al., 1987). The selectivity for K over Ca or Na increases with increasing layer charge in natural smectites (Shainberg et al., 1987) and in smectites with reduced layer charge (Maes & Cremers, 1977, 1978). In contrast, in natural smectites, the layer charge does not affect the Ca-for-Na exchange (Shainberg et al., 1987). Layer charge seems to affect ion exchange by means of steric effects associated with swelling of the smectite layers (Verburg & Baveye, 1994; Laird et al., 1995). However, the preference for a particular cation is associated rather with partition of the cation



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between the aqueous solution and the smectite surface than the selectivity of the surface for a particular cation (Teppen & Miller, 2005; Rotenberg et al., 2009). Yet, although stevensite has lower layer charge than hectorite and saponite, and therefore Na-exchange should have been facilitated, this was not observed in the present study (Table 6).

Charge localization and source of charge are different in the different trioctahedral smectites. Hectorite and stevensite have octahedral layer charge, whereas saponite has tetrahedral layer charge. In addition, the source of charge in hectorite and saponite stems in substitutions within the octahedral sheet (Li for Mg) and the octahedral sheet (Al for Si) respectively, whereas the layer charge of stevensite is due to octahedral vacancies (Brigatti et al., 2013). The surfaces of smectite with tetrahedral charge are more hydrophilic compared to their counterparts with octahedral charge, due to the control of the tetrahedral Al on the maxima and minima of the potential curves on the surface of smectite that affects the hydrophobicity of the surface (Bleam, 1990; Szczerba et al., 2020).

Still, charge localization does not explain the behavior of stevensite, which displayed enhanced Na for Ca exchange only after thermal aging at 230 °C. Indeed, although stevensite and hectorite bear octahedral charge, they displayed different response in Na-exchange at all temperatures except for 230 °C. In both minerals dissolution of dolomite released $Mg^{2+}$ cations to the solution. The different response of stevensite to thermal aging, compared to hectorite, is attributed to the particular nature of this mineral. Most stevensites are actually mixed layer phases, consisting of a swelling phase (stevensite *ss*) and non-swelling kerolite (Eberl et al., 1982, Jones et al., 1984). Although the Moroccan stevensite used in this study does not show evidence of mixed layering (e.g. Christidis & Koutsopoulou, 2013), the small ratio of vacant octahedra, that contribute to the layer charge, to the occupied octahedra (~1:27, c.f. Rhouta et al., 2008), suggests that the uncharged non-swelling kerolite domains (talc like), which have hydrophobic surfaces, promoted particle aggregation. At high temperatures stevensite showed evidence of discrete kerolite-like layers (Fig. 1b). The appearance of discrete kerolitic domains suggests that the charged domains might have been preferentially dissolved, enhancing particle disaggregation through separation of the charged from the uncharged domains, and therefore improving the rheological properties at high temperatures.

Finally, the possibility for crystallization of other phases during high temperature aging, such as analcime or albite (Güven, 1992) and its influence on the rheological properties were not considered in this study because such phases did not form during thermal aging (Fig.1b).

*Use of trioctahedral clays in high temperature drilling muds*

Due to their high dehydroxylation temperatures, trioctahedral clay minerals have higher thermal stability than their dioctahedral counterparts. Therefore, they are possible candidates for the formulation of drilling muds that are employed at high temperature wells, provided that, in the case of smectites, the interlayer cation is Na. All smectites used in this study were Na-activated but only hectorite muds developed satisfactory rheological properties, with the behavior of the remaining clays being unpredictable. The inferior rheological properties of saponite might be attributed to the incomplete Na-exchange, because they are expected to display a greater tendency for adsorbing hydrated cations and swelling, thus facilitating ion exchange, provided that they do not collapse. Yet, after aging the $d_{001}$ of saponite was centered at 13-14 Å and a minor shoulder indicative of Na-layers, appeared at ~12.8 Å (Fig. 1b). The incomplete Na-exchange in the saponite interlayer with respect to hectorite might reflect the influence of charge localization on the exchange. The saponite is dominated by tetrahedral charge. Hence, it may be considered that tetrahedral charge might hinder the Na for Ca exchange. Still, the concentration of $Na_2CO_3$ used to activate the clay was 6%, suggesting that only a fraction of added Na was not exchanged. Therefore, the incomplete Na-exchange cannot explain the inferior rheological properties of saponite.

Although charge localization does not account for the observed incomplete Na-exchange in saponite it may be considered for the interpretation of the rheological properties. Dioctahedral smectites with tetrahedral charge have inferior rheological properties compared to their counterparts with octahedral charge of similar magnitude located in octahedral size (Christidis et al., 2006), because tetrahedral charge will control the maxima of the potential curves on the surface of smectite (Bleam, 1990) that will lead to the aggregation of layers and thus to the suppression of the diffuse double layers. A similar behavior is suggested for the trioctahedral smectites. Therefore, saponites are not expected to develop satisfactory rheological behavior at any temperature, although the tetrahedral charge seems to provide a higher thermal stability against dissolution in the temperature range considered in this study. Still, the rheological behavior might be improved after addition of suitable additives, but this is beyond the scopes of this work.

Stevensite, displayed different rheological behavior than hectorite, although they both have octahedral charge and the layer charge of stevensite is lower than that of hectorite (Christidis & Eberl, 2003; Rhouta et al*.,* 2008). The small ratio of vacant octahedra, that are the source of the layer charge, to the occupied octahedra (~1:27, c.f. Rhouta et al*.,* 2008), suggests that the uncharged non-swelling kerolite domains hinder Na-exchange. Inasmuch as the uncharged kerolite layers are expected to be hydrophobic, similar to talc layers, they impede Na-exchange in the charged layers, causing limited swelling and thus inferior rheological properties. Dolomite dissolution hindered Na-exchange further. The preferential dissolution of the vacant octahedra compared to their occupied counterparts during high temperature aging, facilitated particle separation and thus Na-exchange, thereby promoting Na-





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activation of the stevensite. Therefore, stevensite drilling fluids look promising for high temperature applications.

Hectorite suspensions presented superior rheological performance over all examined clay minerals, even though the content of hectorite in the sample was less than 50%, and dolomite dissolution hindered Na-exchnage. Thermal ageing increased the plastic and apparent viscosity of hectorite suspensions, which demonstrated plastic flow behavior. The extensive gel formation of hectorite suspensions led to the introduction of yield point, which is associated to the hydration of clay particles and the electrostatic interactions among them. The yield point is a function of the number and strength of particle–particle bonds (van Olphen, 1964; Neaman & Singer, 2000b). In addition, hectorite displayed very good thermal stability over the whole temperature range used in this study. Therefore, hectorite is an excellent material for the formulation of drilling fluids for high temperature applications.

The rheological properties of the sepiolite were inferior to those of its bentonite counterparts. The rheological performance of fibrous clays is connected to their fiber length, cation exchange capacity, which is low, and the specific surface area (SSA, Neaman & Singer, 2000a; Simonton et al., 1988). The silanol groups at the external sepiolite surfaces bind the fibrous sepiolite crystals forming networks, thus affecting the apparent viscosity and yield point of sepiolite suspensions (Simonton et al., 1988). However, the sepiolite did not develop suspensions with acceptable rheological behavior and a similar rheological behavior was observed in the preliminary study of a Spanish sepiolite (data not shown). Still, the thermal stability of sepiolite at high temperatures indicates that it might be rendered suitable for high-T drilling applications after the addition of suitable additives. More information about the structural characteristics (e.g., SSA, fiber length etc.) and the use of additives would be necessary.

## CONCLUSIONS

The study examined the influence of thermal aging, up to 230 °C, on 5% suspensions of Mg-bentonites containing trioctahedral smectites (hectorite, stevensite and saponite) after activation with $Na_2CO_3$ and a sepiolite clay, and yielded the following conclusions:

In general, thermal aging did not affect thermal stability of the clays. Except for stevensite clay at 230 °C, the clay minerals displayed minimum dissolution after thermal aging. Hectorite and saponite displayed the best thermal stability at all temperatures, whereas stevensite crystals displayed dissolution features after thermal aging at 230 °C. Thermal stability, recorded as resistance to dissolution, the response to Na-activation and the rheological properties of the clays are directly associated with the crystal structure, namely layer charge and charge localization, the particle shape





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of the clay minerals present and the presence of Mg-accessory minerals that may dissolve during thermal aging like dolomite.

Based on the rheological properties, the sepiolite clay is considered unsuitable for drilling fluids at high temperatures. The rheological properties were almost identical and inferior to bentonites, presenting a subtle, plastic flow behavior at higher temperatures. Moreover, the filtrate loss volume exceeded 15 mL. Also, the saponite clay is not recommended for drilling fluid applications, since it collapses at higher temperatures. Moreover, it did not present acceptable yield point and viscosity, and hence its lubricating, insulating and carrying performance do not meet the API 13A specifications. Nevertheless, the sepiolite and saponite clay suspensions might meet the API 13A specifications if the concentration of solids is raised to 6.42%.

The activation of cation exchange mechanism of stevensite clay at high temperatures makes it a suitable additive for drilling fluids at high temperature operations such as high enthalpy geothermal fields or deep oil well drilling. The intense gel formation leads to high yield point values, which may cause malfunctions to the mud pumps. Consequently, the utilization of stevensite clays in drilling fluid applications is recommended along with other viscosity and gel formation regulating agents.

The hectorite clay displayed excellent rheological properties that did not deteriorate with increasing temperature, although hectorite content was low. Therefore, it is recommended for a wide range of drilling purposes. However, the concentration should remain low, due to the development of viscous fluids with considerable amounts of gel, which may prove stressful for the pumping equipment.

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