Fluid Filtration and Rheological Properties of Nanoparticle Additive and Intercalated Clay Hybrid Bentonite Drilling Fluids

Matthew M. Barry¹, Youngsoo Jung¹, Jung-Kun Lee¹, Tran X. Phuoc^{1,2},
Minking K. Chyu^{1*}

¹*Department of Mechanical Engineering and Materials Science,
University of Pittsburgh, Pittsburgh, PA 15261, USA*

²*National Energy Technology Laboratory, U.S. Department of Energy, Pittsburgh, PA
15236, USA*

Abstract

The fluid filtration and rheological properties of low solid content (LSC) bentonite fluids containing iron-oxide (Fe_2O_3) nanoparticle (NP) additives and two different NP intercalated clay hybrids, iron-oxide clay hybrid (ICH) and aluminosilicate clay hybrid (ASCH), under both low-temperature low-pressure (LTLP: 25 °C, 6.9 bar) and high-temperature high-pressure (HTHP: 200 °C, 70 bar) conditions are investigated. The viscosity of each fluid was measured under LTLP and HTHP conditions using a pressurized and heated rotational viscometer. The LTLP and HTHP fluid filtrate volumes were measured in accordance to American Petroleum Institute standards. The addition of ICH and ASCH into bentonite solutions reduced both LTLP

*Leighton Orr Chair Professor and Chairman and Corresponding author, Ph: 412-624-9720 Fax: 412-624-4846

Email addresses: mmb49@pitt.edu (Matthew M. Barry¹), yoj14@pitt.edu (Youngsoo Jung¹), jul37@pitt.edu (Jung-Kun Lee¹), Phuoc.Tran@netl.doe.gov (Tran X. Phuoc^{1,2}), mkchyu@pitt.edu (Minking K. Chyu¹)

Preprint submitted to Journal of Petroleum Science and Engineering October 28, 2014

and HTHP fluid loss as much as 37% and 47% as compared to the control, under the respective conditions. The pure addition of 0.5 wt.% 3 and 30 nm Fe_2O_3 NP increased the LTLP fluid filtration as much as 14% as compared to the control. However, this addition of Fe_2O_3 NP decreased the HTHP fluid filtrate volumes as much as 28% as compared to the control. It was found the addition of clay hybrids reduced LTLP and HTHP fluid loss due to a restructured mode of clay platelet interaction attributed to a modification in surface charge as demonstrated by zeta potential measurements and scanning electron microscope images.

Keywords: Bentonite solution, drilling fluid, filtration, high-temperature high-pressure, nanoparticle embedded clay hybrids, iron-oxide, low-temperature low-pressure, rheological behavior

1. Introduction

1 Bentonite is a montmorillonite (Mt) clay commonly used in conventional
2 water-based drilling fluids due to inherent, well-performing rheological prop-
3 erties and the vast knowledge thereof [1, 2]. Mt clay solutions exhibit shear-
4 thinning viscosities which provide good pumpability and carrying capacity
5 of cuttings [2]. Additionally, Mt clay forms relatively low permeability filter
6 cakes on the borehole surfaces [3]; thick filter cake formations reduce the
7 effective diameter of the borehole, which causes excessive drag, torque losses,
8 high swab and surge pressures and increases the risk of differential sticking
9 of the drill string [4]. Mt clay begins to chemically break down at tempera-
10 tures as low as 120 °C [5], increasing the drilling fluid loss into sub-surface
11 formations and reducing the effective carrying capacity of cuttings [2], mak-

ing these fluids ineffective for high-temperature and high-pressure (HTHP) drilling applications. High-temperature and high-pressure applications can be classified into three categories, defined by bottom hole temperature (BHT) and pressure (BHP); HTHP when BHT is greater than 150 °C and less than 205 °C or when BHP is greater than 690 bar and less than 1,380 bar; ultra-HTHP when BHT exceeds 205 °C and is less than 260 °C or when BHP exceeds 1,380 bar and is less than 2,410 bar; HTHP-hc when BHT is greater than 260 °C or when BHP is greater than 2,410 bar [6].

To extend the temperature limitation of clay-based drilling fluids, lignite is used within water-based Mt solutions to reduce fluid loss at temperatures up to 177 °C [7]. Above the temperature limitations of lignite-Mt solutions, non-aqueous drilling fluids are preferred in field applications for they are inherently lubricious and provide stable rheological properties up to operating temperatures of 204 °C [8]. However, it is desired to increase the operating limitations of clay-based drilling fluids for HTHP conditions.

To increase the temperature limitation of clay-based drilling fluids, methods have been proposed to modify surface charge to yield lesser fluid filtration loss under HTHP conditions. Haloing stabilizes colloidal fluids such as gels [9], and this study has been extrapolated to surface cation exchange within drilling fluids to promote particular surface structures [10, 11]. The use of organic polymers as viscosifiers suggests cost-effective drilling fluid improvements under HTHP conditions, but such organic polymers also have temperature limitations [12].

It has been demonstrated that micro and nanoparticles (NP) can maintain or increase the performance of drilling fluids under HTHP conditions

[13]. Two methods of micro and NP inclusion into drilling fluids are infusion and intercalation [14, 15]. Infusion is the mere addition of NP into the solution, without much control over the chemical and mechanical interaction between the NP and clay platelet. Micro and NP additives within drilling fluids have the potential to plug pores of subsurface formations, such as shale, preventing drilling fluid loss into said formations and subsurface fluid intrusion into the borehole without compromising the extraction of fluids from the productive horizon [16]. Intercalation is the process of modifying interlaminar cations and neutral species clays, and in this instance, of the Mt aluminosilicates with various alkalies and NP, resulting in permanently charged clay platelets. Intercalation of NP into a host matrix is a widely applied approach for modifying the structure of materials, resulting in improved chemical and physical properties. Inorganic NP have been used to stabilize fluid viscosity at high temperatures via manipulating and modifying the surface morphology and reactivity of the clay platelets [17]. Although much focus has been placed on the rheological properties of intercalated-bentonite solutions [18, 19], current literature does not reflect studies on the fluid filtration losses under LTLP and HTHP conditions.

This work is to address the need of concurrently studying the rheological properties and fluid filtration losses of low-solid content (LSC) bentonite fluids with and without NP additives and embedded clay hybrid solutions under LTLP and HTHP conditions. LSC bentonite fluids with iron-oxide (Fe_2O_3) additives and two different NP embedded clay hybrids are investigated under both low-temperature low-pressure (25 °C, 6.9 bar) and HTHP (200 °C, 70 bar) conditions. The NP embedded clay hybrid solutions of interest are

iron-oxide clay hybrid (ICH) and Al_2O_3 - SiO_2 clay hybrid (ASCH). It will be shown that added ICH and ASCH particles in the LSC bentonite fluid system decreased filtration volumes as compared to a control bentonite solution under LTLP and HTHP conditions due to decreased filter cake permeability. Permeability of the produced filter cake is determined by the mode of interplatelet association. Furthermore, it will be demonstrated the pure addition of Fe_2O_3 NP in concentration of 0.5 wt.% with sizes of 3 and 30 nm had variable effects on fluid loss.

2. Experimental set-up, drilling fluid preparation, and testing

The experiments focused on LTLP and HTHP nanoparticle drilling fluid performance via filtration testing. Low-temperature low-pressure static filtration fluid loss testing was performed in accordance to American Petroleum Institute (API) standards [2, 20, 21]. Figures 1 a) and b) illustrate both the LTLP and HTHP filtration testing system. Five different configurations of drilling fluid solutions were prepared, each made with a five weight-percent (5.0 wt.%) bentonite in deionized water solution, as summarized in Tab. 1; a control of 5.0 wt.% bentonite (Sample A); 5.0 wt.% bentonite solution with 0.5 wt.% 3 nm Fe_2O_3 NP (Sample B); 5.0 wt.% bentonite solution with 0.5 wt.% 30 nm Fe_2O_3 NP (Sample C); 5.0 wt.% bentonite solution with 0.5 wt.% ICH (Sample D); 5.0 wt.% bentonite solution with 0.5 wt.% ASCH (Sample E). Table 6 provides conversions from SI to U.S. customary units.

2.1. Synthesis of nanoparticle-clay hybrids and additive solutions

In this study, two different types of NP-clay hybrid particles were prepared through the intercalation of metal polycations into the interlayer space

86 of the clay and subsequent thermal annealing. The Na^+ -Mt clay (Kunipia F)
 87 used was $\text{Na}_{0.35}\text{K}_{0.01}\text{Ca}_{0.02}(\text{Si}_{3.89}\text{Al}_{0.11})(\text{Al}_{1.60}\text{Mg}_{0.32}\text{Fe}_{0.08})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$.
 88 A detailed synthesis process of the hybrid particle fabrication can be found
 89 in [14] and [22]. A brief description follows here.

90 An iron polycation solution was prepared by dissolving 0.2M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
 91 into 0.4M NaOH at 70 °C. The polycation solution was mechanically mixed
 92 with Na^+ -Mt at the same temperature to yield intercalation. Excessive poly-
 93 cations on the surface of the clay platelets were rinsed with deionized water.
 94 The resulting product was dried and annealed at 450 °C in a N_2 atmosphere
 95 to fully transform intercalated iron polycations to embedded iron oxide NP.

96 The same methodology was employed for the fabrication of Al_2O_3 - SiO_2
 97 NP. ASCH particles were created via obtaining an Al polycation solution
 98 from an aqueous solution of 0.2M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.2M NaOH. Upon twenty-
 99 four hours of mechanical mixing at room temperature, the solution was mixed
 100 with $\text{Si}(\text{OC}_2\text{H}_5)_4$ to make an aqueous hydroxy silico-aluminum polycation so-
 101 lution. The hydroxy silico-aluminum polycation solution was mixed with the
 102 Na^+ -Mt solution, yielding intercalation between the prepared polycations
 103 into the interlayer of the Na^+ -Mt. The hybrid particles were then washed
 104 with deionized water, dried and annealed at 400 °C in a N_2 atmosphere to
 105 fully transform the hydroxy silico-aluminum polycations to embedded alu-
 106 minosilicate NP.

107 To form a 5.0 wt.% bentonite 0.5 wt.% hybrid solution, the hybrid par-
 108 ticles were mixed with bentonite ($\text{H}_2\text{Al}_2\text{O}_6\text{Si}$) in deionized water. These
 109 solutions were mechanically stirred for 30 minutes at 25 °C. Afterwards, the
 110 solutions were sonicated for 30 minutes at 25 °C. The additive NP solutions

were made by the simple mixing and sonication of the aforementioned weight percentages under ambient conditions.

2.2. Rheological testing

A viscometer equipped with a HTHP cell was used to characterize the rheological properties under different shear rates. The viscometer operated at temperatures between 25 °C and 200 °C and pressures between 6.9 bar and 70 bar, coinciding with the LTLP and HTHP filtration environments. The shear rate varied from 1 to 200 s⁻¹ with a step size of 4 s⁻¹. Each step was executed for 10 seconds. Additionally, the zeta potential measurements of the 3 and 30 nm Fe₂O₃ NP solutions were conducted as to determine charge.

2.3. Fluid filtration testing

The LTLP static filtration testing was conducted using a 175 milliliter static filter press with a regulated CO₂ pressurization system and reinforced filter paper. The operating pressure was 6.9 bar and the temperature was atmospheric (25 °C) as to replicate the testing conditions of API fluid-loss testing. The mass of the filtrate was recorded per unit time with a sample rate between five to six measurements per second using a digital balance and a personal computer. The volume was then calculated per the average density of the filtrate collected, which allowed the volume versus time to be determined. The filter cakes were gently rinsed with water to remove any excess fluid and then the thickness was measured using a micrometer.

The HTHP static filtration testing was conducted at 70 bar and 200 °C under a N₂ environment. This system used the same filter press but included

134 a modification to the fluid exit valve in which a two-stage valve and back-
 135 pressure regulator were included. The modification allowed for a continual,
 136 variable back-pressure to be applied on the pressure cell during collection as
 137 to ensure a constant 70 bar pressure differential and to avoid evaporation of
 138 the fluid from the solution until it cooled. Adjustments were made to the
 139 total LTLP and HTHP filtration times as per the recommendation of Arthur
 140 et al. [23]. Each LTLP and HTHP test was conducted three times, with
 141 the average values reported. For HTHP testing, the volume was collected
 142 at 5, 15, 30, 60 and 90 minutes. Filter cake thickness measurements under
 143 HTHP conditions were not conducted due to the damage (dehydration and
 144 cracking) the cake sustained during cooling of the HTHP cell.

145 The undisturbed filter cakes of both LTLP and HTHP samples were then
 146 freeze-dried at -45 °C before being characterized with a field emission electron
 147 microscope. The alignment of the clay platelets was studied using SEM
 148 to observe porous matrix morphology, as has been done in other sources
 149 [24, 25, 26, 27]. Images were taken in the direction of fluid flow.

150 **3. Results and discussion**

151 This section presents the rheological properties and filtration volumes of
 152 various drilling fluids under both LTLP and HTHP conditions. The perfor-
 153 mance of these novel drilling fluids is investigated in comparison to control
 154 of 5.0 wt.% bentonite solution.

155 *3.1. Fluid rheological properties*

156 Drilling fluids are typically characterized as thixotropic shear-thinning
 157 solutions, exhibiting viscosity that decreases with an increase in the shear

158 rate [28]. Additionally, these fluids exhibit a yield stress, or the stress that
 159 must be applied to the fluid to initiate flow, which was found by extrapolating
 160 the shear stress versus shear rate curve to zero-shear conditions. The yield
 161 stress values are reported in Tab. 2. The shear stress versus shear rate plots
 162 for LTLP and HTHP conditions are shown in Fig. 2 a.) and b.).

163 Evaluating the drilling fluid as a Herschel-Bulkley fluid, the shear stress
 164 τ is

$$\tau = \tau_y + K\dot{\gamma}^n \quad (1)$$

165 where τ_y is the yield stress, K is the flow consistency index, $\dot{\gamma}$ is the shear
 166 rate in s^{-1} and n is the flow behavior index. The flow consistency K and flow
 167 behavior index n were found by fitting the shear stress versus shear rate data
 168 to a two-equation yield power law (Herschel-Bulkley) with 95% confidence
 169 bounds. The flow consistency and behavior indices are presented in Tab. 2
 170 with the yield stress.

171 It is noted from Fig. 2 a) that the 3 and 30 nm Fe_2O_3 and ICH solutions
 172 exhibit a yield stress, then a decrease in stress with an increase in shear rate
 173 until a flow point is reached. This indicates the fluid appears to be in solid-
 174 like elastic state. After the flow point, the stress versus shear rate behaves
 175 according to the Herschel-Bulkley model, that is, the fluid has transitioned
 176 to a liquid-like viscous state. This is attributed to the complex interparticle
 177 interaction of additive Fe_2O_3 NP and ICH particles within the bentonite
 178 solution, which is elaborated upon in the following paragraphs. The values
 179 for yield stress presented in Tab. 2 with parentheses indicating the modified
 180 yield stress (flow point) for which the fluid was fitted.

181 The ICH and additive Fe_2O_3 NP solutions have greater viscosities whereas
182 the ASCH has a lower viscosity as compared to the bentonite control under
183 LTLP conditions. Under HTHP conditions, the ICH solution has a greater
184 viscosity whereas the Fe_2O_3 additive and ASCH solutions have a lower vis-
185 cosity as compared to the bentonite control. The viscosity of each fluid
186 is attributed to the mode of clay platelet interaction as brought about by
187 surface charges, either through the addition of Fe_2O_3 NP or through the
188 introduction of intercalated clay platelets.

189 The addition of ICH particles into the bentonite solution promoted at-
190 traction of positives charges on the surfaces of the hybrid clay platelet with
191 the negative charges of the bentonite platelets. This attraction was between
192 the edge of the ICH particle and the face of a non-hybrid bentonite clay
193 platelet (E-F) as well as attraction between the face of the hybrid iron-oxide
194 clay platelet and the face of the non-hybrid clay platelet (face-to-face (F-F)
195 flocculation), resulting in the formation of a rigid 3D clay platelet network.
196 This network can be seen in Fig. 4 b.) and is graphically illustrated in the
197 panel below image b.). This rigid clay platelet network increased the viscos-
198 ity of the fluid and the resistance to flow as evidenced through an increase
199 in the yield stress by nearly one order of magnitude, as compared to the
200 bentonite control [14].

201 In contrast, embedded Al_2O_3 - SiO_2 nanoparticles promoted negative charges
202 at the edge of the ASCH particle, increasing the negativity of the net charge
203 of the hybrid particle. This resulted in the generation of repulsive forces
204 between hybrid ASCH and bentonite clay platelets in the fluid system. This
205 strong electrostatic repulsion prevented coagulation and the subsequent for-

206 mation of a strong clay platelet network. This formation is illustrated in
 207 Fig. 4 c.) and is graphically illustrated in the panel below image c). Even
 208 under HTHP conditions, where typical disassociation of Na^+ ions within the
 209 bentonite leads to flocculation and an increase in the viscosity of the fluid
 210 system [18, 19, 34], ASCH prevented this flocculation of clay platelets, yield-
 211 ing a well-dispersed fluid, as evidenced by a reduction in the flow stress as
 212 compared to the bentonite control [14].

213 The addition of Fe_2O_3 NP induced heterocoagulation, or the assembly
 214 of different types of clay particles in a collective behavior through the in-
 215 troduction of an electrolyte to the clay solution, promoting a rigid structure
 216 [11, 29, 30] and a stronger gel formation [14, 31]. This yielded an increase in
 217 viscosity and flow stress under LTLP conditions in comparison to the ben-
 218 tonite control, indicating flocculation through edge-to-edge (E-E) and edge-
 219 to-face (E-F) associations. Flocculation was induced due to the imbalance
 220 of electrical charges on the surface of the clay platelet, as seen in the SEM
 221 images in Figs. 4 d.) and e.) and graphically illustrated in the panel between
 222 images d.) and e.). The Fe_2O_3 NP exhibit positive charges in an aqueous
 223 environment and will attract the negatively charged faces of the bentonite
 224 clay platelets. Under HTHP conditions, the viscosity and flow stress of the
 225 Fe_2O_3 solutions minimally increased in comparison to the bentonite control,
 226 indicating flocculation via the same associations between edge and face as
 227 seen under LTLP conditions [14].

228 It is evident the addition of 0.5 wt% 3 nm Fe_2O_3 NP had a more substan-
 229 tial effect on viscosity and flow stress of the bentonite solution than did the 30
 230 nm counterpart. The viscosity increased 194% and 40% in comparison to the

231 bentonite control for the 3 nm samples under LTLP and HTHP conditions,
 232 respectively, in comparison to the 66% and 5% increase in LTLP and HTHP
 233 viscosities of the 30 nm samples. The flow stresses increased on the same
 234 order of magnitude as the viscosities for both samples under both conditions
 235 in comparison to the control [14]. The reason for an increase in viscosity and
 236 flow stress is how the NP associate with the clay platelets, with themselves,
 237 and the subsequent interaction between clay platelets, as evidenced by zeta
 238 potential (ZP) measurements.

239 The 3 and 30 nm Fe_2O_3 NP with concentration of 5 mg/1 mL in DI
 240 water with a pH of 8.2-8.6 have ZP values of 15.22 ± 0.78 and 17.44 ± 0.42
 241 respectively, indicating unstable colloidal solutions with a high potential of
 242 aggregation (in the chemistry definition). Stable colloidal solutions typically
 243 have absolute ZP values greater than 30. In 5.0 wt.% bentonite solution, the
 244 0.5 wt.% 3 and 30 nm Fe_2O_3 solutions have ZP values of -23.50 ± 1.73 and -
 245 7.53 ± 2.00 mV and pH values of 8.64 and 8.82. In comparison, the ZP of the
 246 5.0 wt.% bentonite solution was found to be -7.06 ± 2.64 . Typically, there is a
 247 large negative charge generated in aqueous Mt solutions due to substitution
 248 of Si^{4+} for Al^{3+} , Mg^{2+} , and Fe^{2+} in the Mt aluminosilicate layers. However,
 249 based on the magnitude of the ZP for the 5.0 wt.% bentonite solution, there
 250 is not enough electrostatic repulsion within the colloidal solution to keep
 251 it well-dispersed, hence the onset of flocculation. The larger magnitude of
 252 the ZP of the 3 nm Fe_2O_3 NP solution indicates greater stability than the
 253 bentonite control and 30 nm Fe_2O_3 solution.

254 The relative stability of the 3 nm Fe_2O_3 NP solution is due to the larger
 255 surface area to volume ratio of the 3 nm Fe_2O_3 NP as compared to the 30 nm

256 Fe_2O_3 NP. A larger surface area to volume ratio leads to stronger electrical
257 attraction with the negatively charged face of the bentonite clay platelet.
258 Furthermore, for the same weight percent, there are more 3 nm Fe_2O_3 NP
259 participating in attraction with the bentonite clay platelet. Additionally, the
260 3 nm Fe_2O_3 NP experience aggregation between NP due to electrostatic
261 attraction. The mutual attraction between NP and clay platelet surfaces
262 results in a heterocoagulated structure as seen in bottom middle panel of Fig.
263 4. The 3 nm Fe_2O_3 heterocoagulated bentonite clay platelets are positively
264 charged, repelling like structures and platelets within the solution and thus
265 the solution exhibits better dispersion (higher ZP value) and stability than
266 the 30 nm Fe_2O_3 and bentonite solutions.

267 The pH values of the 3 and 30 nm Fe_2O_3 NP solutions are 8.64 and 8.82.
268 Lower pH values (<7.5) lead to E-E and E-F flocculation due to the min-
269 imization of surface charge imbalance [32]. Increasing the pH leads to an
270 increase in F-F associations, where the clay platelets aggregate, forming a
271 linked structure [33]. This linked structure is able to trap more water between
272 the layers, increasing the viscosity, yield stress and subsequently decreasing
273 fluid filtration volume. The addition of the 3 and 30 nm Fe_2O_3 NP did not
274 substantially affect the pH of the solution as to increase E-E or E-F flocculation,
275 nor did they induce F-F flocculation. Thus, the heterocoagulated
276 structure increased the viscosity and yield stress, and as will be presented in
277 the following section, LTLP fluid filtration loss.

278 Increasing the temperature and pressure of the drilling fluid changes the
279 viscosity, and thus the rheological properties and subsequent fluid filtration
280 performance. It has been proposed that elevated temperatures induce the

281 dissociation of Na^+ from the surface of bentonite, leading to an increase in
 282 viscosity [18, 19, 34], as evidenced by Figs. 3 a) and b). For example,
 283 Samples A through E experienced an 18.9-, 9.0-, 11.9-, 5.5-, and 5.1-fold
 284 increase in apparent viscosity when tested under HTHP as compared to LTLP
 285 conditions, respectively. The effect of pressure, although acting to increase
 286 the viscosity via increased particle interaction, is not as great as temperature
 287 [35, 36]. From prior work, it can be seen that the effect of pressure is less
 288 than temperature on the viscosity of bentonite, ICH and ASCH solutions [14].

289 3.2. Fluid filtration properties

290 3.2.1. LTLP

291 Figure 5 depicts the behavior of the entirety of the bentonite solutions
 292 fluid filtrate loss per unit square-root of time in comparison to the control
 293 under LTLP conditions. Table 3 summarizes the filtration volumes of the flu-
 294 ids under both LTLP and HTHP conditions. The fluid filtrate loss is plotted
 295 against the square root of time for the solution of Darcy’s Law (Eqn. 2) is in
 296 the form of Eqn. 3 and additionally, after the spurt loss, the fluid filtrate loss
 297 becomes linear with respect to the square root of filtration time. Fitting the
 298 filtration volume versus times as per the power law yields exponent values in
 299 the range of 0.49 to 0.51 as seen in Tab. 4, which do not reflect the idealized
 300 value of 0.5 from Darcy’s Law.

301 The ICH and ASCH fluids exhibit the least fluid loss, respectively. The
 302 ICH and ASCH solutions exhibited a 37% and 19%, 36% and 18%, and
 303 34% and 17% reduction in 30-, 60- and 90-minute fluid filtration volumes
 304 as compared to the 5.0 wt.% bentonite, respectively. Darcy’s Law describes
 305 fluid filtrate volumes dV as a function of time dt , cross-sectional area A ,

306 permeability κ , pressure differential ΔP , viscosity η and filter cake thickness
 307 t_c , which is expressed as

$$\frac{dV}{dt} = \frac{\kappa \Delta P A}{\eta t_c}. \quad (2)$$

308 The solution to Darcy's Law as a function of the aforementioned variables
 309 is expressed as

$$V_f = A \sqrt{\frac{2t\kappa\Delta P}{\eta} \left(\frac{f_{sc}}{f_{sm}} - 1 \right)}, \quad (3)$$

310 where f_{sm} is the volume fraction of solids within the mud and f_{sc} is the
 311 volume fraction of solids within the cake. To calculate the permeability of
 312 each solution's filter cake, the following assumptions were made; the cross-
 313 sectional area is constant at 45 cm²; the pressure difference is constant at 6.9
 314 bar; the viscosity of the fluid of interest is water taken at 25 °C; the filter
 315 cake thickness, although a function of time, is assumed constant and is taken
 316 as the reported final measured thickness as seen in Tab. 5.

317 It is evident from Tab. 5 that the permeability of the additive 3 and 30
 318 nm Fe₂O₃ filter cakes prepared under LTLP conditions are 66% and 26%
 319 higher than the bentonite control, respectively. As observed from Fig. 5, the
 320 additive Fe₂O₃ NP bentonite solutions increased fluid loss as compared to
 321 the control, which is attributed to the increase in permeability of the filter
 322 cake due to the hetercoagulated structure. Additionally, an increase in fil-
 323 trate volume would yield an increase in filter cake thickness as seen in Tab. 5.
 324 While the size of the Fe₂O₃ NP increased from 3 to 30 nm, the solution ex-
 325 hibited a small decrease in fluid filtrate volume which is attributed to a slight

326 decrease in filter cake permeability. The heterocoagulated formation, which
327 formed a strong clay platelet network, did not experience compaction during
328 filtration testing, thus the high permeability filter cake. As the particle size
329 increased, the degree of heterocoagulation decreased, reducing the filter cake
330 permeability and filtrate volume.

331 The ICH and ASCH solutions produced filter cakes of lesser permeability
332 which reflect a 17% and 23% reduction in κ in comparison to the bentonite
333 control, as provided in Tab. 5. The embedded Fe_2O_3 NP promoted posi-
334 tive charges at the edge of the particles, bringing about strong attractive
335 forces between the positively charged edge of ICH particles and negatively
336 charged face of clay particles, exhibiting a house-of-cards structure. Strongly
337 cross-linked formations provide more rigid structure which exhibit apparent
338 low permeability, explaining a decrease in the filtrate volumes. In contrast,
339 embedded $\text{Al}_2\text{O}_3\text{-SiO}_2$ NP promote negative charges at the edge of the parti-
340 cle, leading to a repulsive force between ASCH and bentonite clay platelets.
341 This electrostatic repulsion prevented clay platelet coagulation, and addi-
342 tionally maintained a well-dispersed fluid. The permeability decreased due
343 to subsequent compaction of the well-dispersed, non-coagulated platelets,
344 as evidenced by the filter cake thickness which was less than the bentonite
345 control, yielding a reduction in filtrate volume.

346 The effect of intercalation and additive NP is illustrated by the SEM
347 images in Fig. 4. Figure 4 a) shows the control bentonite filter cake, whereas
348 Figs. 4 b) and c) show the ICH and ASCH filter cakes. The ICH filter
349 cake exhibits predominant F-F association through electrostatic attraction
350 between the face of the hybrid iron-oxide clay platelet and the face of the

351 non-hybrid clay platelet. This resulted in the formation of a rigid 3D clay
352 platelet network, which increased the resistance to flow and decreased the
353 permeability. The ASCH filter cake as seen in Fig. 4 c) is the result of a
354 strong cross-linked clay platelet network formation that is a result of strong
355 electrostatic repulsion between ASCH and bentonite clay platelets. This
356 strong network formation reduced the porosity and subsequent permeability.

357 Figures 4 d.) and e.) shows the SEM images, concurrent with literature
358 [37], and the schematic illustration representing hetercoagulated formations
359 of Fe_2O_3 NP and clay platelets. Randomly shaped and empty spaces are
360 created between the particles and thus filtration easily occurs through these
361 pores, leading to higher permeability values and fluid filtrate volumes.

362 3.2.2. *HTHP*

363 Figure 6 a.) and b.) depict the behavior of the hybrid (ICH and ASCH)
364 and 3 and 30 nm additive Fe_2O_3 bentonite solutions fluid filtrate loss per
365 unit square-root of time under HTHP conditions, respectively, along with
366 the results being summarized in Table 3.

367 The ICH and ASCH added fluids exhibit the least fluid loss in comparison
368 to the bentonite control, with a reduction in fluid filtrate volumes by 47% and
369 20% for the 30-minute, 43% and 23% for the 60-minute and 35% and 26% for
370 the 90-minute tests, respectively. With an increase in temperature, the ICH
371 filter cake retained the strong positive charges, which attracted the negative
372 charges on the faces of the bentonite platelets, thus creating a rigid house-of-
373 cards structure with a high viscosity. The house-of-cards structure allowed
374 for the formation of a filter cake with low-permeability characteristics. The
375 permeability of the ICH filter cake was decreased due to reduced pore sizes,

376 which is attributed to the collapse of the hybrid and non-hybrid clay platelets
377 via the strong attraction between hybrid and bentonite platelets faces (F-
378 F). This low porosity and low permeability filter cake exhibited low filtrate
379 volume in comparison to the bentonite control.

380 The negative charge of the ASCH clay platelets repulsed the bentonite
381 clay platelets and acted as a deflocculant, promoting clay platelet dispersion
382 within the solution at elevated temperatures [2, 14]. This dispersion resulted
383 in the production of a low porosity and low permeability filter cake, resulting
384 in lesser fluid filtrate volume as compared to the bentonite control.

385 Figure 6 b.) depicts the filtration volumes of bentonite fluids containing
386 Fe_2O_3 additive NP under HTHP conditions. Contrasting to the indications
387 in Fig. 4, under HTHP conditions, Fe_2O_3 additive NP solutions showed
388 a decrease in fluid filtration volume as compared to the control bentonite
389 fluid. Elevated temperatures induce flocculation of clay platelets and the
390 dissociation of Na^+ from the surface of bentonite; as Na^+ concentrations
391 increase, pre-existing network formations collapse and the solution became
392 flocculated, creating a high porosity and high permeability filter cake, as
393 evidenced by a 330%, 286% and 246% increase in the 30-, 60- and 90-minute
394 HTHP filtration volumes of the 5.0 wt% bentonite solution as compared to
395 LTLP. However, the Fe_2O_3 NP replaced the disassociated Na^+ and allowed
396 the clay platelet to retain a positive charge along the edge; this retention
397 of positive edge charge kept the clay platelets dispersed and deflocculated.
398 Thus, the deflocculated solution exhibit a low porosity and low permeability
399 filter cake, thus less filtrate volume in comparison to the bentonite control.

400 The filter cake permeability and subsequent fluid filtration is influenced

by the clay platelet interaction under HTHP conditions; ICH added solutions exhibit rigid networks and low permeability filter cakes due to the strong network formation between positively charged hybrid platelets and negatively charged bentonite edges, thus low filtration volumes; ASCH added solutions exhibit good dispersion due to repulsion generated between negatively charged hybrid particles and negatively charged bentonite faces, thus minimal clay platelet network formation and low permeability filter cakes; additive Fe_2O_3 solutions are deflocculated due to the replacement of dissociate Na^+ cations with Fe_2O_3 NP, leading to a solution that yield low permeability filter cakes.

This work illustrates how modifying the surface charge of clay-based drilling fluids via intercalation and NP addition can alter the rheological properties and fluid filtration characteristics of conventional drilling muds under LTLP and HTHP conditions.

4. Conclusions

The rheological properties and fluid filtration performance of low solid content bentonite fluids containing iron-oxide (Fe_2O_3) additives and nanoparticle (NP) intercalated clay hybrids under low-temperature low-pressure (LTLP: 25°C, 6.9 bar) and high-temperature high-pressure (HTHP: 200°C, 70 bar) conditions were investigated.

The iron-oxide clay hybrid (ICH) added hybrid solution exhibited less fluid filtrate as compared to the bentonite control under LTLP and HTHP conditions. ICH added solutions exhibited strong cross-linked and coagulated platelet networks under LTLP and HTHP conditions. The cross-linked

425 platelet network was less sensitive to pressure and temperature which re-
426 sulted in less permeable filter cakes, reducing fluid filtrate volumes under
427 LTLP and HTHP conditions.

428 The LTLP and HTHP fluid filtrate volumes of the aluminosilicate clay
429 hybrid (ASCH) added hybrid solutions were less than the bentonite control
430 due to the reduced permeability of the filter cakes. The effect on permeability
431 is attributed to the strong electrostatic repulsion between the hybrid particles
432 and clay platelets which provided good dispersion and prevented coagulation
433 and flocculation.

434 The pure addition of 0.5 wt.% 3 and 30 nm Fe_2O_3 NP in 5.0 wt.% ben-
435 tonite solutions increased the fluid filtrate volume under LTLP conditions as
436 compared to the 5.0 wt.% bentonite control. Fe_2O_3 NP promoted hetercoag-
437 ulation of clay platelets which resulted in the formation of a permeable filter
438 cake during filtration testing. Furthermore, the pure addition of Fe_2O_3 NP
439 to the bentonite solution tested under HTHP reduced fluid filtrate volumes
440 as compared to the bentonite control. The fluid filtrate volume decreased at
441 elevated temperatures because Fe_2O_3 NP replaced dissociated Na^+ cations,
442 deflocculating the solution which yielded a low permeability filter cake

443 SEM images of the Fe_2O_3 additive solutions showed rigid, porous struc-
444 tures under LTLP conditions and less porous structures under HTHP con-
445 ditions. SEM images of the ICH added solution filter cakes showed a semi-
446 porous cross-linked structure under both LTLP and HTHP conditions, and
447 those of the ASCH added solutions filter cakes showed random, coagulated
448 structures under both LTLP and HTHP condition.

449 Nomenclature

450 Variables

A	area, m ²
t_c	cake thickness, m
K	flow consistency index, Pa-s
n	flow behavior index, dimensionless
451 ΔP	pressure differential, Pa
t	time, s
T	temperature, °C
V	volume, mL

452 Greek symbols

η	flow behavior index, dimensionless
453 $\dot{\gamma}$	shear rate, s ⁻¹
κ	permeability, D
τ	shear or yield stress, Pa

454 Subscripts

30	30-minute
60	60-minute
455 90	90-minute
c	cake, m
y	yield

456 5. Acknowledgements

457 This work was supported by the Department of Energy.

Table 1: Abbreviated Sample Names.

Sample	Sample Abbreviation
5.0 wt.% Bentonite	Sample A
5.0 wt.% Bentonite with 0.5 wt.% 3 nm Fe ₂ O ₃	Sample B
5.0 wt.% Bentonite with 0.5 wt.% 30 nm Fe ₂ O ₃	Sample C
5.0 wt.% Bentonite with 0.5 wt.% ICH	Sample D
5.0 wt.% Bentonite with 0.5 wt.% ASCH	Sample E

Table 2: The yield stress τ_y , flow consistency index K and flow behavior index n of all drilling fluids under LTLP conditions treated as Herschel-Bulkley fluids.

Sample	τ_y [Pa]	K [Pa-s]	n
A	1.04	0.022 ± 0.001	0.890 ± 0.001
B	$2.43 (1.436 \pm 0.046)$	0.060 ± 0.007	0.742 ± 0.020
C	$2.03 (1.403 \pm 0.026)$	0.033 ± 0.003	0.817 ± 0.015
D	$9.85 (3.165 \pm 1.411)$	3.041 ± 1.07	0.225 ± 0.040
E	0.25	0.011 ± 0.002	0.856 ± 0.030

Table 3: LTLP and HTHP fluid filtrate volumes V (all volumes are in [mL] and are reported at time in minutes).

		Sample A	Sample B	Sample C	Sample D	Sample E
LTLP	V_{30}	9.6	10.7	9.8	6.1	7.8
	% Change	–	+11.5	+2.1	-36.5	-18.8
	V_{60}	13.4	12.6	13.9	8.6	11.0
	% Change	–	-6.0	+3.7	-35.8	-17.9
	V_{90}	16.0	18.3	17.0	10.6	13.3
	% Change	–	+14.4	+6.3	-33.8	-16.9
HTHP	V_{30}	41.0	29.7	31.4	21.6	32.9
	% Change	–	-27.6	-23.4	-47.3	-19.8
	V_{60}	51.6	40.4	42.3	29.6	39.7
	% Change	–	-21.7	-18.0	-42.6	-23.1
	V_{90}	55.5	47.5	49.3	35.9	40.9
	% Change	–	-14.4	-11.2	-35.3	-26.3

Table 4: Exponential fit of filtration data under LTLP and HTHP conditions.

Sample	LTLP	HTHP
A	$0.49 \pm 1\text{e-}4$	0.40 ± 0.127
B	$0.50 \pm 1\text{e-}4$	0.50 ± 0.078
C	$0.51 \pm 1\text{e-}4$	0.32 ± 0.105
D	$0.51 \pm 1\text{e-}4$	0.48 ± 0.101
E	$0.49 \pm 1\text{e-}4$	0.44 ± 0.034

Table 5: Permeability κ calculated from Darcy’s Law from filter cake thicknesses t_c under LTLP conditions.

Sample	t_c [cm]	κ 10^{-3} [mD]
A	3.82	3.33
B	5.55	5.53
C	4.53	4.18
D	4.82	2.77
E	3.54	2.57

Table 6: Conversion between metric and U.S. customary units

Physical Quantity	Metric Units	U.S. Customary Units
Length	1 m =	39.3701 inches
Pressure	1 bar =	14.5038 psi
Temperature	1 °C =	(°F - 32) $\cdot \frac{5}{9}$
Viscosity	1 Pa-s =	24.1909 pound/foot-hour
Volume	1 mL =	0.0338 fluid ounce

458 **References**

- 459 [1] P. F. Luckham, S. Rossi, *The colloidal and rheological properties of ben-*
460 *tonite suspensions*, Advances in Colloid and Interface Science 82 (13)
461 (1999) 43-92.
- 462 [2] A. T. Bourgoyne Jr., M. E. Chenevert, K. K. Millheim, F. S. Young
463 Jr., Applied Drilling Engineering, vol. 2, Society of Petroleum Engineers,
464 1986.
- 465 [3] D. H. Larsen, *Use of clay in drilling fluids*, Clay and Clay Technologies
466 (1955) 269-281.
- 467 [4] H. Darley, G. R. Gray, *Composition and properties of drilling and com-*
468 *pletion fluids*, Gulf Professional Publishing, 5 edn., 1988.
- 469 [5] V. C. Kelessidis, C. Tsamantaki, N. Pasadakis, E. Repouskou, E. Hami-
470 laki, *Permeability, porosity and surface characteristics of filter cakes from*
471 *water bentonite suspensions*, 6th International Conference on Advances in
472 Fluid Mechanics, 2006.
- 473 [6] A. Belani and S. Orr, *Management-A Systematic Approach to Hostile*
474 *Environments*, Journal of Petroleum Technology, 60 (7) (2008).
- 475 [7] V. C. Kelessidis, C. Tsamantaki, A. Michalakis, G. E. Christidis, P. Makr,
476 K. Papanicolaou, A. Foscolos, *Greek lignites as additives for controlling*
477 *filtration properties of water-bentonite suspensions at high temperatures*,
478 Fuel 86 (78) (2007) 1112-1121.

- 479 [8] M. Mas, T. Tapin, R. Mácrquez, R. Gabay, Z. Negrín, C. Díaz, L. Be-
480 jarano, *A new high-temperature oil-based drilling fluid*, Latin American
481 and Caribbean Petroleum Engineering Conference, Society of Petroleum
482 Engineers, 1999.
- 483 [9] V. Tohver, J. E. Smay, A. Braem, P.V. Braun, J. A. Lewis, *Nanoparticle*
484 *halos: a new colloid stabilization mechanism*, Proceedings of the National
485 Academy of Sciences 98 (16) (2001) 8950-8954.
- 486 [10] E. Tombácz, J. Balázs, J. Lakatos, F. Szántó, *Influence of the exchange-*
487 *able cations on stability and rheological properties of montmorillonite sus-*
488 *pensions*, Colloid and Polymer Science 267 (1989) 1016-1025.
- 489 [11] E. Tombácz, C. Czanaky, E. Illés, *Polydisperse fractal aggregate forma-*
490 *tion in clay mineral and iron oxide suspensions, pH and ionic strength*
491 *dependence*, Colloid and Polymer Science 279 (2001) 484-492.
- 492 [12] V. Mahto, V. Sharma, *Rheological study of a water based oil well drilling*
493 *fluid*, Journal of Petroleum Science and Engineering 45 (12) (2004) 123-
494 128.
- 495 [13] J. C. Baird and J. Y. Walz. *The effects of added nanoparticles on aque-*
496 *ous kaolinite suspensions: II. Rheological effects*, Journal of Colloid and
497 Interface Science 306 (2) (2007) 411-420.
- 498 [14] Y. Jung, Y.-H. Son, J.-K. Lee, T. X. Phuoc, Y. Soong, M. K. Chyu,
499 *Rheological behavior of clay nanoparticle hybrid-added bentonite suspen-*
500 *sions: specific role of hybrid additives on the gelation of clay-based fluids*,
501 ACS Applied Materials and Interfaces 3 (9) (2011) 3515-3522.

- 502 [15] T. Huang, J. B. Crews, G. Agrawal, *Nanoparticle psuedocrosslinked mi-*
 503 *cellar fluids: optimal solution for fluid-loss control with internal break-*
 504 *ing*, SPE International Symposium and Exhibition on Formation Damage
 505 Control, Society of Petroleum Engineers, 2010.
- 506 [16] J. T. Srivatsa, M. B. Ziaja, *An experimental investigation on use of*
 507 *nanoparticles as fluid loss additives in a surfactant-polymer based drilling*
 508 *fluids*, International Petroleum Technology Conference, 2012.
- 509 [17] T. Huang, J. B. Crews, *Nanotechnology applications in viscoelastic sur-*
 510 *factant stimulation fluids*, SPE Production and Operations 23 (4) (2008)
 511 512-517.
- 512 [18] E. Tombácz, M. Szekeres, *Colloidal behavoir of aqueous montmoril-*
 513 *lonite suspensions: the specific role of pH in the presence of indifferent*
 514 *electrolytes*, Applied Clay Science 27 (12) (2004) 75-94.
- 515 [19] S. Laribi, J.-M. Fleureau, J.-L. Grossiord, N. Kbir-Ariguib, *Effect of*
 516 *pH on the rheological behavior or pure and interstratified smectite clays*,
 517 Clays and Clay Minerals 54 (1) (2006) 29-37.
- 518 [20] Spec 13A, Specification for Drilling-Fluid Materials, American
 519 Petroleum Institute, Production Department, Washington, DC, 15 edn.,
 520 1993.
- 521 [21] Recommended practice standard procedure for laboratory testing
 522 drilling fluids, API recommended practice, American Petroleum Insti-
 523 tute, Production Department, Washington, DC, 1990.

- 524 [22] Y.-H. Son, J.-K. Lee, Y. Soong, D. Martello, M. Chyu, *Structure prop-*
 525 *erty correlation in iron oxide nanoparticle clay hybrid materials*, Chem-
 526 *istry of Materials* 22 (7) (2010) 2226-2232.
- 527 [23] K. Arthur, J. Peden, *The evaluation of drilling fluid filter cake properties*
 528 *and their influence on fluid loss*, International Meeting on Petroleum
 529 *Engineering*, Society of Petroleum Engineers, Tianjin, China, 1988.
- 530 [24] K. E. Porte, *A basic scanning electron microscope study of drilling fluids*,
 531 *SPE Formation Damage Symposium*, Society of Petroleum Engineers,
 532 1980.
- 533 [25] L. Hartmann, M. Özerler, C. Marx, H.-J. Neumann, *Analysis of mud-*
 534 *cake structures formed under simulated borehole conditions*, *SPE Drilling*
 535 *Engineering* 3 (4) (1988) 395-402.
- 536 [26] J. Plank, A. Trostberg, F. Gossen, *Visualization of fluid-loss polymers in*
 537 *drilling-mud filter cakes*, *SPE Drilling Engineering* 6 (3) (1991) 203-208.
- 538 [27] M. Chenevert, J. Huycke, *Filter cake structure analysis using the scan-*
 539 *ning electron microscope*, Tech. Rep., Society of Petroleum Engineers,
 540 1991.
- 541 [28] S. Livescu, *Mathematical modeling of thixotropic drilling mud and crude*
 542 *oil flow in wells and pipelinesA review*, *Journal of Petroleum Science and*
 543 *Engineering* 98 (2012) 174-184.
- 544 [29] U. Brandenburg, G. Lagaly, *Rheological properties of sodium montmo-*
 545 *rillonite dispersions*, *Applied Clay Science* 3 (3) (1988) 263-279.

- 546 [30] G. Lagaly, *Principles of flow of kaolin and bentonite dispersions*, Applied
547 Clay Science 4 (2) (1989) 105-123.
- 548 [31] I. C. Callaghan, R. H. Ottewill, *Interparticle forces in montmorillonite*
549 *gels*, Faraday Discuss. Chem. Soc. 57 (1974) 110-118.
- 550 [32] J. Stawinski, J. Wierzechos and M. T. García González, *Influence of*
551 *calcium and sodium concentration on the microstructure of bentonite and*
552 *kaolin*, Clays and Clay Minerals 38 (1990) 617-622.
- 553 [33] H. Vali and L. Bachmann. *Ultrastructure and flow behavior of colloidal*
554 *smectite dispersions*, Journal of Colloid and Interface Science 126 (1)
555 (1988) 278-291.
- 556 [34] M. Ramos-Tejada, F. Arroyo, R. Perea, J. Durán, *Scaling behavior of the*
557 *rheological properties of montmorillonite suspensions: correlation between*
558 *interparticle interaction and degree of flocculation*, Journal of Colloid and
559 Interface Science 235 (2) (2001) 251-259.
- 560 [35] N. J. Alderman, A. Gavignet, D. Cuillot, G. C. Maitland and others,
561 *High-temperature high-pressure rheology of water-based muds*, SPE An-
562 nual Technical Conference and Exhibition, Society of Petroleum Engi-
563 neers, 1988.
- 564 [36] B.J. Briscoe, P. F. Luckham, and S. R. Ren, *The properties of drilling*
565 *muds at high pressures and high temperature*, Philosophical Transactions
566 of the Royal Society of London. Series A: Physical and Engineering Sci-
567 ences 348 (1687) (1994) 179-207.

- 568 [37] H. van Olphen, *Internal mutual flocculation in clay suspensions*, Journal
569 of Colloid Science 19 (4) (1964) 313-322.

570 Figure Captions

- 571 1. Low-temperature low-pressure and high-temperature high-pressure fil-
572 tration testing assemble with a) HTHP experimental set-up and b)
573 schematic of LTLP and HTHP equipment.
- 574 2. Shear stress vs. shear rate of various drilling fluids under a.) LTLP
575 and b.) HTHP conditions. Solid lines indicate Herschel-Bulkley fits,
576 based upon the information provided in Tab. 2.
- 577 3. Viscosity vs. shear rate of various drilling fluids under a.) LTLP and
578 b.) HTHP conditions.
- 579 4. SEM of LTLP filter cakes: a.) Sample A b.) Sample D c.) Sample E
580 d.) Sample B e.) Sample C with corresponding clay platelet interaction
581 illustrations.
- 582 5. Cumulative LTLP fluid filtration volumes as a function of square-root
583 of time.
- 584 6. Cumulative a.) hybrid and b.) additive HTHP fluid filtration volumes
585 as a function of square-root of time.

Figure 1

Figure 2a

Figure 2b

Figure 3a

Figure 3b

Figure 4

Figure 5

Figure 6a

Figure 6b