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HP-HT Drilling Mud Based on Environmentally-Friendly Fluorinated Chemicals

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Abstract — *The worldwide growing demand for energy drives oil and gas companies to drill deeper and hotter wells. The exploration and the development of Deeply Buried Reservoirs (DBR) generate major technical challenges due to the extremely high pressures and temperatures met (1 400 bar, 300°C). Currently, several drilling fluids are emerging. They are briefly reviewed at the beginning of the paper. The technical difficulty related to HP-HT mud is so significant that standard mud formulation technologies are irrelevant and alternative systems have to be considered. New formulations based on perfluorochemicals have been jointly developed by IFP Energies nouvelles (IFPEN), Solvay Specialty Polymers Italy and Total. Their lab characterizations are presented and reveal their promising benefits.*

Résumé — **Boues de forage HP/HT à base de composés fluorés respectueux de l'environnement**
— La demande croissante en énergie pousse les entreprises pétrolières et gazières à forer de plus en plus profond. L'exploration et l'exploitation des gisements très enfouis (*Deeply Buried Reservoirs*, DBR) génèrent des défis techniques importants en raison des pressions extrêmement élevées et des températures rencontrées (1 400 bar, 300 °C). Actuellement, plusieurs fluides de forage sont mis sur le marché. Ils sont brièvement passés en revue au début du manuscrit. La difficulté technique liée à la boue HP-HT est telle que les technologies habituelles de formulation de boues sont inadaptées et des systèmes alternatifs doivent être considérés. De nouvelles formulations à base de composés perfluorés ont été développées conjointement par *IFP Energies nouvelles (IFPEN)*, *Solvay Specialty Polymers Italy* et *Total*. Leurs caractérisations en laboratoire sont présentées et montrent leur potentiel.

INTRODUCTION

The worldwide growing demand for energy drives oil and gas companies to drill deeper and hotter wells. The exploration and the development of Deeply Buried Reservoirs (DBR) generate major technical challenges due to the extremely high pressures and temperatures met (1 400 bar, 300°C). Such severe conditions demand careful attention to select efficient mud systems. Actually, drilling muds are a key factor in drilling operations. They are used to:

- maintain pressure balance between formation and the borehole;
- lift cuttings to the surface;
- cool and lubricate the drill bit;
- seal permeable formations;
- stabilize the borehole.

Currently, several drilling fluids are emerging. They are mainly of three types: Oil-Based Muds (OBM), Water-Based Muds (WBM) and formate brines. They are briefly discussed at the beginning of the paper with their own pros and cons. The technical difficulty related to HP-HT mud is so significant that alternative systems have to be considered. Therefore new formulations have been jointly developed by *IFPEN*, *Solvay Solexis* and *Total*. The formulations for this application were patented by *IFPEN* under patent US7858564 [1]. Then the composition was optimized and made subject-matter of an international patent application filed in collaboration with *Solvay Specialty Polymers Italy* and *Total* and published as WO2012010530 [2]. They are based on perfluorochemicals whose technology is described in Section 2 of the paper. Final systems have been formulated to cover a density range up to 2.2 SG, a thermal stability after prolonged exposure up to 300°C and a low viscosity. Their lab preparation and their physicochemical characterization are detailed in the main text of the document.

1 LITERATURE OVERVIEW OF RECENT HP-HT MUDS

As mentioned above, there are three main categories of muds used to drill in extreme conditions. Each of them are under constant and advanced research to adapt and improve performance. The articles cited below are some examples of experimental work focusing on the methods to increase the thermal stability of muds. They encompass insightful lab studies and exploratory field cases covering severe HP-HT conditions up to 315°C (600°F) and 2 757 bar (40 000 Psi).

1.1 Oil-Based Muds (OBM)

Traditionally OBM also called invert emulsions are preferably used to drill deep wells. Actually, their characteristics

address technical requirements (good lubricating properties, low fluid loss, adequate filter cake) and they are supposed to show superior temperature stability when compared with WBM. According to Lee *et al.* [3], most of the invert drilling fluids can handle temperatures up to 205°C (400°F) without significant issues. These authors extended this limit up to 315°C (600°F) by using unspecified products. In the same manner, Moura *et al.* [4] successfully applied a paraffin-based HP-HT fluid for an offshore exploration well (169°C, 336°F) in Brazil. The mud was designed to meet the operational requirements by blending it with an unspecified HP-HT stabilizer and organophilic clays as gelling and suspending agents. The same kind of mud containing modified clays was recently employed with standard API barite (BaSO₄) to drill an exploration well in East Malaysia [5]. Standard barite was introduced as a weighting agent with an appropriate emulsifier package to avoid its sagging. Another option to limit the settling phenomenon is to choose ultra-fine barite [6]. Barite is commonly preferred due to its abundance. Nevertheless, it is criticized due to its high contents in heavy metals such as lead, cadmium, mercury and arsenic [7]. Rehman *et al.* [8] reported the development of an oil based mud weighted by manganese tetraoxide (Mn₃O₄) particle instead of barite. They are environmentally friendly (belonging to OCNS group D or E) and advantageously prevent sagging thanks to their inherent sub-micron size. They also exhibit an excellent spherical shape that leads to lower viscosity and reduced abrasion risk.

In sum, the thermal stability of OBM can be substantially improved by the selection of appropriate chemical additives. Anyhow they can be regarded as undesirable from an economic and environmental point of view [9, 10]. They also present the serious disadvantages of adsorbing a large amount of gas [11] and impairing the logging interpretation [12].

1.2 Water-Based Muds (WBM)

Despite their technical performance, OBM may be discarded due to environmental and cost constraints. As a result, operators may have to choose WBM systems. To fill the technical gap between both drilling fluids, new WBM have been designed through extensive studies. Some illustrative examples are given below in the particular case of HP-HT applications. The typical composition of aqueous drilling systems comprises biopolymers (xanthan, scleroglucan gum) or synthetic polymers (polyelectrolytes). High molecular weight polymers are used to give the required rheology while low molecular weight ones are used for fluid loss control. A weighting material is added to adapt density. Tehrani *et al.* [13] developed a new water based drilling fluid relying on the synergy between the weighting agents (manganese

tetraoxide or barite) and the selected polymers (modified acrylic polymers and polyvinylpyrrolidone). The system showed good thermal stability up to 180°C. Sun *et al.* [14] reported the development of a water based organosilicon drilling system that was used in the deep Qingshen gas field at 220°C. Their formulation includes highly charged ion complexes that adsorb on clay and improve their water retaining capacity. A thick hydration film is formed around clay particles and is said to limit water loss in HT conditions. Recently Elkatatny *et al.* [15] evaluated a water-based drilling fluid with micronized ilmenite instead of barite with correct drilling properties up to 177°C.

WBM are not as thermal resistant as oil based ones. Special chemicals may improve their performance so that they can be selected for some severe drilling operations but not all. Most of the water soluble polymers used (biopolymers and polyelectrolytes) are sensible to hydrolysis and thermal degradation. Moreover according to Hassiba and Amani [16] the use of water based drilling fluids may be challenged by the high probability to encounter salt beds in deep wells. Salt contamination may alter their rheological properties and saturated brines may have to be used.

1.3 Formate Brines

The use of sodium, potassium and cesium formate brines as drilling and completion HP-HT fluids is relatively new and has been the subject of an abundant literature [17, 18]. The interest for these products is supported by their natural density and their thermal stability. Formate compounds are the salts of formic acid and are easily dissolved in water. Their chemical description can be found in Javora *et al.* [19]. The exact formulation of a formate mud depends on the target density and does not require the addition of weighting solids. They are compatible with elastomers. In the mid-90s, sodium formate and potassium formate brine became popular, and replaced halide brine, chlorides and bromides. Advantages of formate brine were a less corrosive environment for the metals, a less harmful fluid for personnel and the environment. Cesium formate had difficulty to be introduced into the market due to its price and scarce availability. In the late 90s oil and gas operators started using the high density Cesium Formate as a completion fluid, replacing Calcium Bromide/Zinc Bromide brines, which were practically banned from North Sea applications.

A review of operator's feedbacks from long term use was recently published by Olvik *et al.* [20]. It underlines the drilling benefits and their operational success. To reduce the negative impact of cost, formate systems can be recovered at the end of each job and recycled [21]. Despite many advantages, formate muds are challenged because they might affect standard nuclear logging tools [22].

2 TECHNOLOGY DESCRIPTION OF FLUORINATED POLYMERS AND SURFACTANTS

2.1 PFPE Polymers and Surfactants

PerFluoroPolyEthers (PFPE) are fluorinated fluids that are known for their unique physical and chemical properties. Actually, they exhibit both an excellent thermal stability and a high chemical resistance. They are transparent colourless and odourless oils, which remain liquid in a wide range of temperatures. They are very dense and non-flammable polymers with a low interfacial energy. Due to these numerous advantageous properties, PFPE are used in various high tech applications such as high quality lubrication [23, 24]. PFPE have been commercially available worldwide for long, especially in the form of neutral end-capped fluids. The pioneers of these technological polymers were *Solvay Specialty Polymers Italy (Montedison at that time) (Fomblin® PFPE)* and *Du Pont (Krytox® PFPE)* in the 1960s.

Solvay Specialty Polymers Italy is the largest supplier of PFPE fluids with the widest product range in the world. Technology is based on photooxidation of perfluoroalkenes as described in several articles and papers [25-27]. PFPE are divided into two groups of structure: the branched and the linear ones. Their respective structures and preparations are given below.

Branched Fomblin® Y PFPE are prepared by reaction of HexaFluoroPropene (HFP) and oxygen catalyzed by UV light through several steps: the intermediate polyperoxide (I) is then reduced to get rid of the peroxide bonds, leading to a polyether with acid fluoride end groups (II), which are removed by fluorination with elemental fluorine under UV conditions (Fig. 1). In the chain the ratio p/q is about 40, which means more units $-CF_2CF(CF_3)O-$ than $-CF_2O$.

Linear Fomblin® Z are prepared with almost the same process but starting from TetraFluoroEthylene (TFE) (Fig. 2); in this case the ratio p/q is about 0.5-2.

For both processes, the final products can be further fractionated to obtain the suitable grades. Actually, versatility is another attribute of the PFPE compounds, which results in additional benefits to design engineers. The molecular structure of the polymer chain, that is how the C, F, O atoms are linked is the attribute responsible for this broad range of features. Typical properties of PFPE fluids are presented in Table 1. They show the key role played by the structure of the PFPE backbone.

Branched structure (Fomblin® Y PFPE) shows higher values for the Tg and a greater dependence of the viscosity with the temperature due to the presence of bulky pendant $-CF_3$ groups which causes stiffening of the polymer chain.

On the contrary the linear structure (Fomblin® Z PFPE) shows a lower decrease in the viscosity with temperature and the lowest values of the pour point due to presence of the $-CF_2O$ units which increases the degree of flexibility of the molecule, thus showing that the increase in the O/C

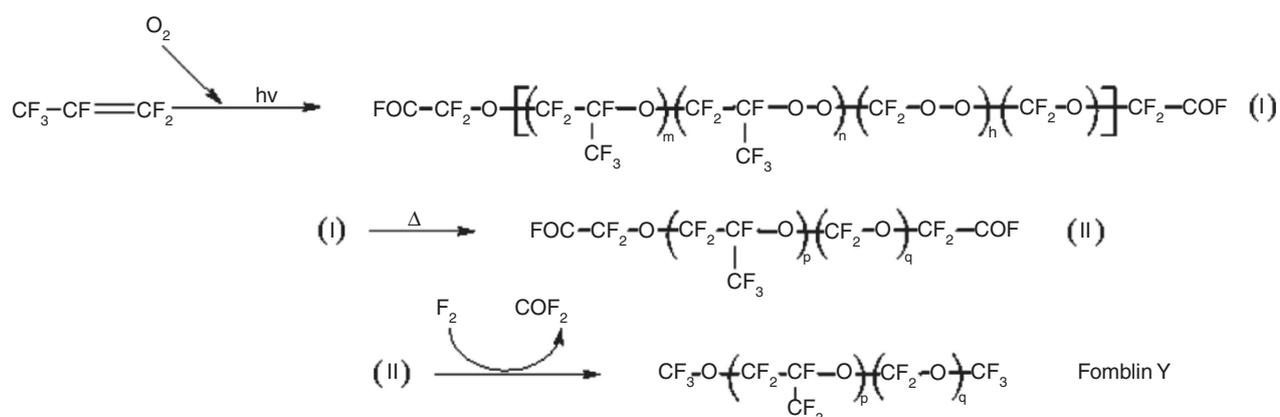


Figure 1

Preparation of Fomblin® Y.

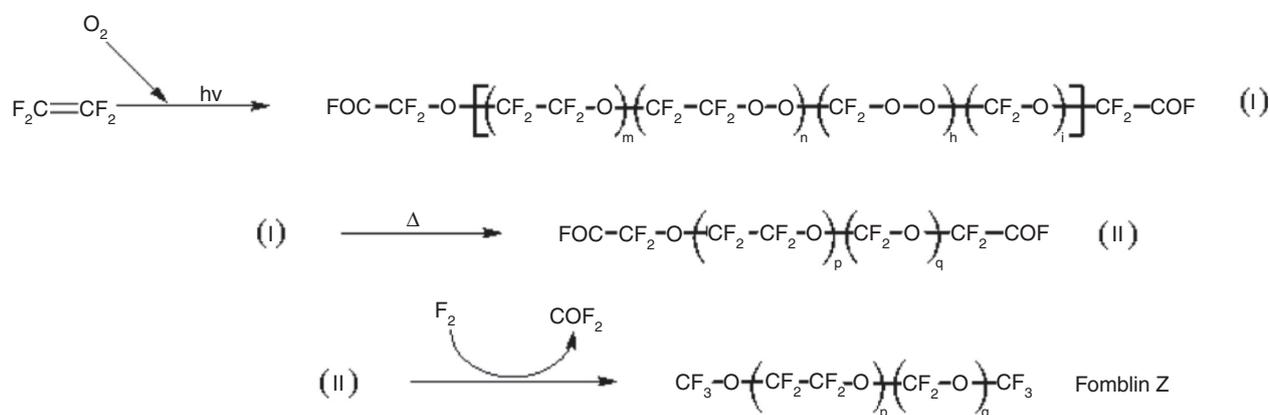


Figure 2

Preparation of Fomblin® Z.

TABLE 1
Properties of PFPE

Fomblin® type	Average mol. weight	Kinematic viscosity			Viscosity index	Pour point	Density at 20°C	Tg
		20°C	40°C	100°C				
	(amu)	(cSt)	(cSt)	(cSt)	(-)	(°C)	(g/cm ³)	(°C)
Y	1 500	38	15	3.2	60	-58	1.87	-57
	3 200	250	80	10	108	-35	1.90	
	4 100	470	147	16	117	-35	1.97	
	6 250	1 300	345	33	135	-30	1.91	
	7 250	1 850	510	47	135	-25	1.92	
Z	4 000	30	17	5	253	-85	1.81	-130
	8 000	150	85	22	286	-75	1.83	
	11 000	280	159	45	338	-65	1.85	
	16 000	550	310	86	343	-60	1.86	
	23 000	1 300	700	200	375	-50	1.87	

ratio is a key parameter for this property. The variation of the viscosity with temperature and pressure for PFPE (Tab. 1) has been extensively studied and reported by many authors [28-32].

The C-F chemical bond is the strongest inter-atomic bond found in nature, while at the same time, electronegative fluorine forms a barrier against reagent aggression. The absence of hydrogen also contributes to the stability of PFPE fluids. Therefore, these polymers are chemically inert and resistant to the majority of reagents including mineral acids, alkalis, organic acids and bases, oxidizing and reducing agents and halogens. No reaction or change in the fluid is observed for prolonged exposition to very aggressive chemicals even at high temperatures. They can only be affected by direct contact with strong electropositive metals like Na, Al, Mg or can undergo a decomposition catalyzed by Lewis acids like $AlCl_3$ or SbF_3 .

2.2 Functional PFPE and their Applications

An additional development is the production of functionalized PFPE, in particular the bifunctionalized ones known with the trade name of Fluorolink[®]. Several structures and properties are reported in Table 2.

PFPE structures may be linked to a large variety of functional groups, either reactive or not. This allows providing compounds which perform better in the typical applications of these fluids, and to extend their use to new applications through the proper selection of specific functional groups [33, 34]. For example functionalized PFPE can be used as

surfactants in emulsion and microemulsion technologies [35-37]. These formulations can be employed to cover surface as treatment to impart oleo/hydrophobicity and lubricity to various materials (such as metal, fibers, etc.), or in cosmetic application, etc.

Properties of the selected PFPE for the Mud formulations

Among the various functionalized PFPE, Table 3 lists the ones that have been selected for the mud formulation. The selection was driven to reach a given range of density, of viscosity and thermal stability, as will be explained in the following section.

3 HP-HT FLUORINATED MUD

3.1 Mud Formulation

The dense polymer Fomblin[®] Y04 PFPE ($d = 1.9$) was selected to form the continuous phase of the mud. This choice was based on two additional characteristics:

- a high thermal resistance;
- a moderate viscosity due to its lower molecular weight.

The liquid cannot itself constitute a drilling mud. It is necessary to control the mud during drilling either in

TABLE 2
Typical properties of Fomblin[®] PFPE derivatives $XCF_2O-[(CF_2CF_2O)_p(CF_2O)_q]-CF_2X$

Trade name	X			
	-CO ₂ H	-CH ₂ (OCH ₂ CH ₂) _n OH	-CH ₂ OH	-(OCH ₂ CH ₂) _n -OPO(OH) ₂
Fluorolink [®] properties	C10	E10H	D10H	F10
M _w (amu)	1 500	1 500	1 500	2 000
Fluorine content (%)	59	57	61	50
Viscosity (cSt) at 20°C	60	115	85	3×10^4 - 1×10^5
Density (g/mL)	1.80	1.73	1.79	1.70-1.80
Surface tension (dyne/cm) at 20°C	22	23	24	n.a
Refractive index $n_{D_{20}}$	1.300	1.317	1.302	n.a
Glass transition (T_g , °C)	-110	-100	-95	n.a
Vapour pressure (mmHg) at 20°C	2×10^{-5}	n.a	7×10^{-5}	n.a
Vapour pressure (mmHg) at 100°C	2×10^{-3}	n.a	5×10^{-3}	n.a

TABLE 3
Properties of selected PFPE

PFPE type	Average mol. weight (amu)	Density (g/mL) at 20°C	Kinematic viscosity (cSt)		
			20°C	40°C	100°C
Fomblin® Y25	3 200	1.90	250	80	10
Fomblin® Y04	1 500	1.87	38	15	3.2
Fomblin® Y 2045X	1 984	1.87	62.7	25.3	4.49
Fluorolink® F10	2 000	1.70-1.80	3×10^4 - 1×10^5	na	na

TABLE 4
Typical composition of HP-HT synthetic mud

Ingredient	Concentration	Function
Fomblin® Y04 PFPE	73.6% vol	Continuous phase
Fluorolink® F10 PFPE	0.4% vol	Emulsifier and wetting agent
Brine (CaCl ₂ 300 g/L; pH = 10)	10% vol	Internal phase for suspension properties and density decrease
Barite (8 μm)	16% vol	Weighting agent for suspension properties and density increase

increasing its density by adding weighting agents or reducing it by adding a less dense aqueous phase. Therefore one must disperse both phases homogeneously so as to avoid sedimentation. Initial tests showed settling when adding micron sized barite in a PFPE. In order to disperse the weighting agents and the internal aqueous phase within the polymeric liquid, perfluoropolyether surfactants containing different functionalities have been screened. Fluorolink® F10 PFPE was found to be the best candidate. Actually, thanks to two terminal phosphate groups, this product shows good wetting and emulsifying properties. Due to its PFPE composition, it is all the more dense ($d = 1.73$) and thermal resistant. A typical composition of the developed mud is indicated in Table 4.

In order to adapt the formulation to both viscosity and density requirements, and considering the viscosity of the starting PFPE liquid, it is possible to tune the formulation. The volume fraction of weighting agent and of brine are adjusted obeying two constraints. It is necessary to stabilize the weighting agent suspension, helped by the presence of the brine emulsified in the PFPE continuous phase. It is also necessary for the mud to flow properly. Thereby the viscosity must not exceed a certain threshold, thus limiting the volume fraction of all the dispersed objects *i.e.* weighting agent particles and emulsified brine droplets. Figure 3 illustrates the influence of barite and brine volume fraction upon the density of the mud and its relative viscosity $\eta_R = \eta/\eta_0$ with η_0 being the viscosity of the initial PFPE liquid.

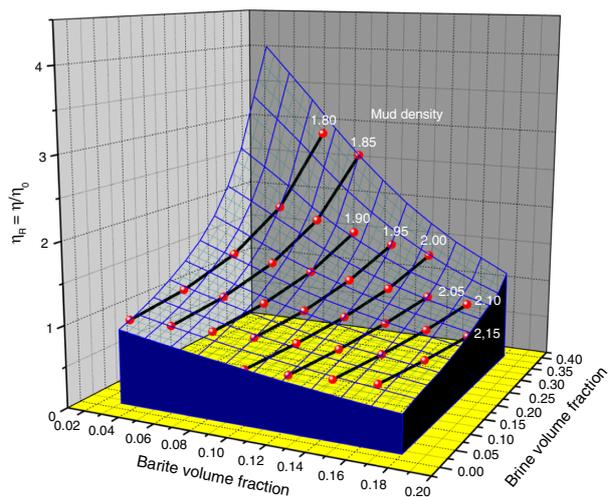


Figure 3

Influence of formulation parameters on both density and relative viscosity of the mud.

The ingredients were mixed using a Ultra Turrax® T25 homogenizer. To prepare a 200 mL sample, the ingredients were introduced as follows:

1. introduction of Fomblin® Y04 polymer (279.7 g);
2. introduction of Fluorolink® F10 polymer (1.384 g) and stirring during 5 minutes;
3. introduction of brine (22.4 g) and stirring during 15 minutes;



Figure 4

Innovative synthetic fluorinated mud (Fomblin® Y04 and Fluorolink® F10 PFPE).

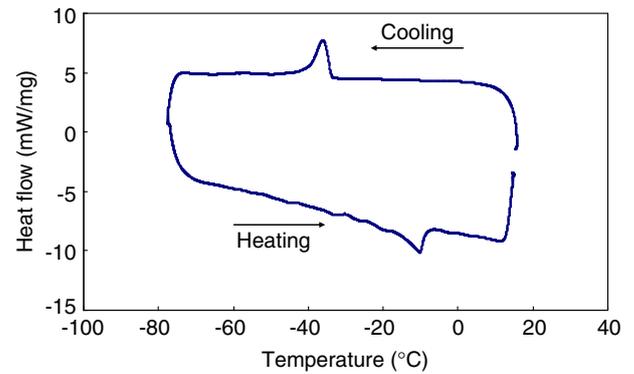


Figure 5

Cooling and heating thermographs of the HP-HT fluorinated mud (Fomblin® Y04 and Fluorolink® F10 PFPE).

4. introduction of barite (standard granulometry 8 μm) (134.4 g) and stirring during 15 minutes.

During all the above steps, rotational speed was set at 11 000 rpm while temperature was maintained at ambient. The resulting mud can be seen in Figure 4.

The formulation described above underwent a comprehensive battery of laboratory tests to determine its performance. They include:

- a basic characterization at atmospheric pressure (Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), viscosity measurements, electrical conductivity and shear resistance);
- tests under HP-HT conditions (viscosity and thermal resistance);
- resistance to influx (liquid hydrocarbons, gas and water).

3.2 Mud Characterization at Atmospheric Pressure

3.2.1 DSC and Cryogenic SEM Analysis

DSC can be advantageously used to characterize the aqueous internal phase of a drilling fluid. This analytical technique consists of measuring the heat exchanges between the sample and a reference either *versus* time at constant temperature or *versus* temperature during a heating or a cooling program. It allows determining the emulsion type, the amount of water, the presence of solute, the stability and the droplet size [38].

The thermograms obtained with the formulated mud are shown in Figure 5. The cooling part comprises a

single regular exothermic peak at around -35°C . This signal is characteristic of a fine and monodisperse emulsion. Actually, according to nucleation theory, the freezing temperature may be correlated to the mean droplet size of the emulsion [38]. The very low peak indicates that the formulated mud comprises micro-sized droplets. During heating, an endothermic peak relates to the progressive melting of the ice. It is observed around -10°C , which corresponds to the liquid/salt equilibrium temperature of the brine.

The DSC analysis confirms that the HP-HT fluorinated mud contains the required internal aqueous phase. Moreover, it can be noted that this phase is dispersed in micron size droplets, that favors the emulsion stability.

To cross check the DSC characterization, microscopic analysis were performed with cryogenic SEM on the fluorinated mud. The SEM results confirmed the small size of emulsion and the good dispersion of mineral particles. In addition, SEM provided the elemental composition of the sample. Figure 6 is an example of barium (barite particles) and chlorine (brine) analysis which confirms the size of the particles and good morphology of the mud.

3.2.2 Rheological Characterization

Rheological characterization was carried out using the controlled stress rheometer *Haake 150* with a 40 mm sanded plate geometry. The flow curves showed that the HP-HT fluorinated mud has the required rheological properties of a drilling mud:

- a yield stress;
- a shear thinning behaviour.

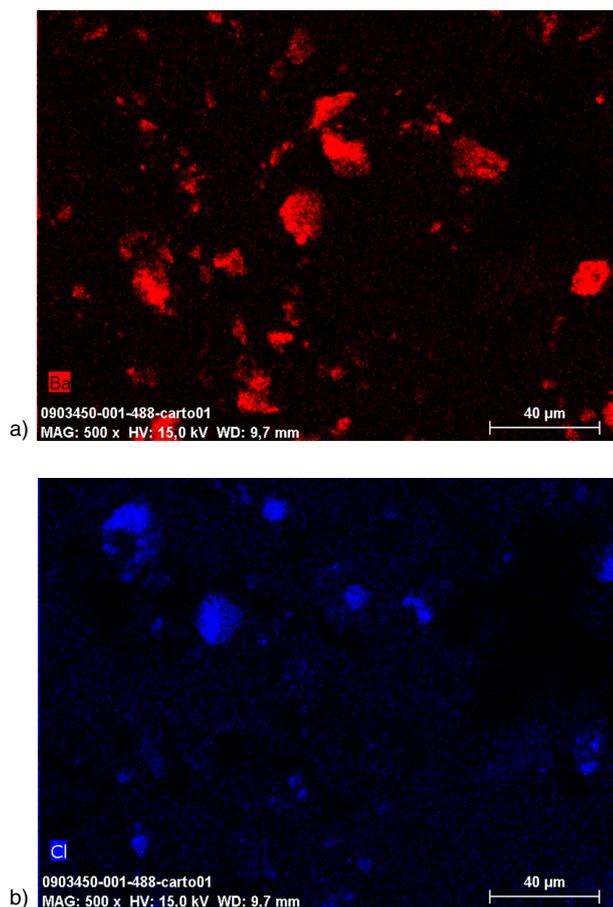


Figure 6

Cryo-SEM elemental analysis of the HP-HT fluorinated mud (Fomblin® Y04 and Fluorolink® F10 PFPE); a) barium, b) chlorine.

The responses have been fitted with the Herschel-Bulkley model:

$$\tau = \tau_{y0} + k\dot{\gamma}^n$$

with: τ , shear stress (Pa); $\dot{\gamma}$, shear rate (s^{-1}); τ_{y0} , yield shear stress (Pa); k , consistency; n , power law exponent.

The model coefficients for different temperatures are presented in Table 5. The viscosity measured at around $500 s^{-1}$ is also indicated. When plotted as a function of temperature, it obeys the Arrhenius law with an activation energy equal to 24 kJ/mol. This result shows that the viscosity of the fluorinated HP-HT mud has a classical thermal dependency.

3.2.3 Settling Tests

The settling tests consist of monitoring the extent of phase separation with time. It is carried out with a Turbiscan™ LAB

TABLE 5
Rheological properties of the HP-HT fluorinated mud

	τ_{y0} (Pa)	k	n	η (cp) at $500 s^{-1}$
20°C	3	0.44	0.92	280
30°C	2.3	0.26	0.93	180
50°C	1.9	0.14	0.93	93
80°C	1.6	0.07	0.93	50

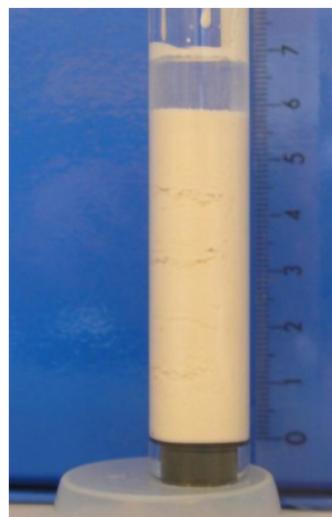


Figure 7

HP-HT synthetic mud (Fomblin® Y04 and Fluorolink® F10 PFPE) (1/3 standard and 2/3 fine barite) after complete settling.

apparatus that acquires transmission and backscattering data every 40 μm while moving along the 55 mm cell height. The acquisition along the product is then repeated with a programmable frequency to obtain product profiles and reveal the stability or instability of the product. The extent of phase separation in static conditions was estimated at around 45%. It can be mentioned that the supernatant phase is clear and transparent. IR and DSC analysis have been performed on it. They reveal that it does not contain any water nor solid particles.

The previous settling tests have been repeated on a reformulated mud. It contains alternative weight materials composed of 1/3 of standard barite (8 μm) and 2/3 of fine-grind barite (2 μm) in weight. The results show that the partial addition of fine barite limits the extent of the settling to 15% after 24 hours (Fig. 7).

Rheological measurements were performed on the mud containing partly fine barite. Its viscosity is only slightly increased compared to that of the initial mud. The addition

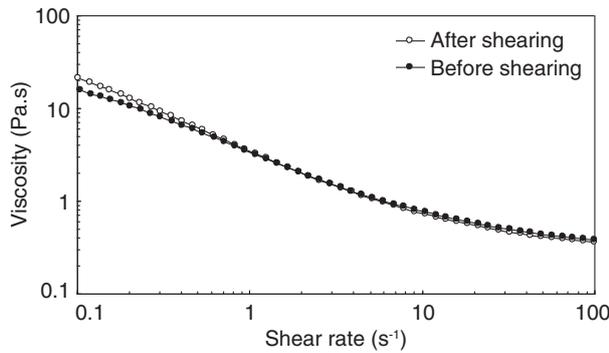


Figure 8

Viscosity at 20°C of the HP-HT fluorinated mud (Fomblin® Y04 and Fluorolink® F10 PFPE) before and after shearing.

of fine barite improves the settling properties of the mud without being detrimental to its flow behaviour.

3.2.4 Electric Conductivity

Electric conductivity of the HP-HT fluorinated mud (Fomblin® Y04 and Fluorolink® F10 PFPE) has been measured using *Metrohm 712* conductimeter with an open geometry measurement cell. A value of 210 $\mu\text{S/m}$ was found at ambient temperature. According to Sawdon *et al.* [39], this value is within the desirable range for electrical logging operations (10–10³ $\mu\text{S/m}$).

3.2.5 Shear Resistance

During drilling operations, the mud must sustain strong mechanical solicitations. In order to quantify the mechanical resistance of the new synthetic mud, the formulation was sheared with a *Ultra Turrax® T25* homogenizer during 4 hours at 11 000 rpm. The flow curve of the sheared sample was measured at 20°C and compared to the one of the unsheared blank (Fig. 8). These curves are exactly the same, showing that the mud is resistant to mechanical shearing.

3.3 Mud Characterization under HP-HT Conditions and Thermal Resistance

3.3.1 Rheological Behavior under HP-HT Conditions

The rheological behavior of a first fluorinated mud was characterized under HP-HT conditions. This mud had the same composition as the one given in Table 4, except it contains Fomblin® Y25 PFPE as base polymer. The tests were performed on a *Fann 70* rheometer with temperature ranging from 75 to 200°C and pressure ranging from 1 to 1 330 bar. The resulting flow curves showed that the mud is

Newtonian, with a viscosity remaining constant as the shear rate changes. When plotted as a function of pressure, viscosity increases exponentially obeying Barus' law:

$$\kappa = \frac{d \ln \eta}{dP}$$

κ is the piezoviscous coefficient which value strongly depends upon temperature. It can be mentioned that pressure effect on viscosity strongly diminishes at high temperature. Actually, in deep conditions, viscosity will be mostly governed by temperature.

The HP-HT rheology of a second fluorinated PFPE mud (Fomblin® Y04 and Fluorolink® F10 PFPE) was also characterized. Results are given in Table 6. They were entered into a proprietary simulator and Equivalent Circulating Densities (ECD) were calculated (Fig. 9) with the following conditions:

- drilling fluid: 2.12 sg,
- bit depth: 7 019 m,
- flow rate: 1000 L/min,
- pipe rotation: 110 rpm,
- rate of penetration: 2 m/h,
- frac pressure: 2.29 sg EMW (Equivalent Mud Weight) at 6250 mTVD (True Vertical Depth).

The results show that a drilling fluid designed with a base fluid Fomblin® Y04 PFPE is compatible with drilling operations in an HP-HT type well.

3.3.2 Thermal Resistance

In order to test their thermal resistance, several PFPE mud samples were introduced into sealed gold tubes placed inside an autoclave (Fig. 10). This set up enabled to heat the samples at temperatures up to 300°C during 24 hours, with an external pressure of 100 bar.

After heating at 250°C during 24 hours, the phase separation appears with the same extent as the one previously determined at 25°C with a *Turbiscan™* apparatus. A gentle stirring is enough to disperse the settled phase (Fig. 11).

Once the mud is homogenised, flow curves were measured and compared to the original ones (Fig. 12). They almost superimpose, which demonstrates the thermal stability of the fluorinated muds.

To confirm the thermal resistance, microscopic analysis were performed with cryogenic SEM on the heated fluorinated mud (Fomblin® Y04 and Fluorolink® F10 PFPE). The morphology they revealed is the same as the original sample (Fig. 13). Despite having undertaken a severe heating, samples still contain well dispersed water droplets and barite particles.

The two previous fluorinated muds have been tested in more severe thermal conditions: they have been introduced in sealed gold tubes and placed in an autoclave at 300°C for 24 hours. Pictures of the resulting products are shown

TABLE 6
HP-HT rheology of PFPE mud (Fomblin® Y04 and Fluorolink® F10 PFPE)

Shear rate		Pression (psi)	FANN 75 readings												
rpm	s ⁻¹		0	0	0	3 000	6 000	6 000	9 000	9 000	12 000	12 000	15 000	12 000	15 000
Temperature (°C)		25	50	65	80	80	120	120	155	155	180	180	200	200	
600	1 022	300	179	113	186	221	145	213	100	191	101	138	61	86	
300	511	246	83	70	104	146	81	104	68	102	65	93	32	41	
200	341	192	58	55	78	110	63	79	55	79	53	72	25	29	
100	170	105	37	37	49	68	43	51	40	51	38	49	18	21	
60	102	56	29	29	36	49	33	38	33	39	31	39	17	18	
30	51	32	23	24	27	34	27	30	29	30	27	31	15	16	
6	10	11	9	14	16	21	23	23	19	20	19	20	12	15	
3	5	8	7	13	14	18	18	22	15	18	10	14	10	10	

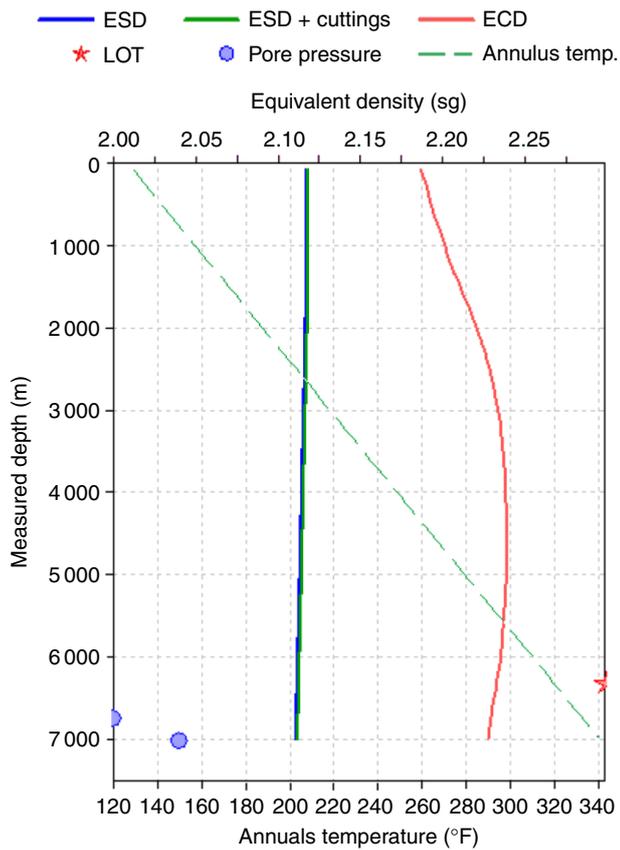


Figure 9
ECD simulation for PFPE mud (Fomblin® Y04 and Fluorolink® F10 PFPE).

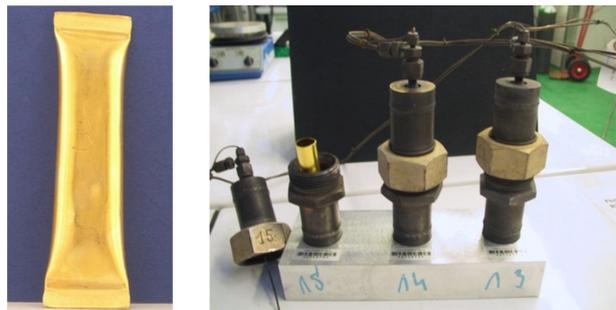


Figure 10
Gold tube and autoclave used to heat the PFPE mud.

in Figure 14. The two muds prepared with PFPE keep their fluidity despite the harshness of the thermal treatment.

3.4 Resistance to Formation Fluid Influxes

In case of unexpected fluid influxes in a well or “kick”, mixing between mud and formation fluids can take place and affect mud properties. Fluorinated muds present the significant advantage of not adsorbing either hydrocarbon or aqueous fluids, thus preventing the mud from being impacted. This immiscibility between mud and formation fluids also favours kick detection. These important assets are illustrated in the next paragraphs successively detailing the resistance of fluorinated muds to hydrocarbon, gas and water influxes.

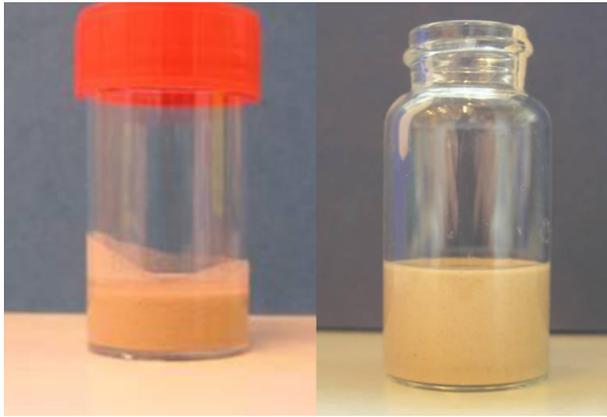


Figure 11

HP-HT Fluorinated mud (Fomblin[®] Y04 and Fluorolink[®] F10 PFPE) after having been exposed to 250°C during 24 hours.

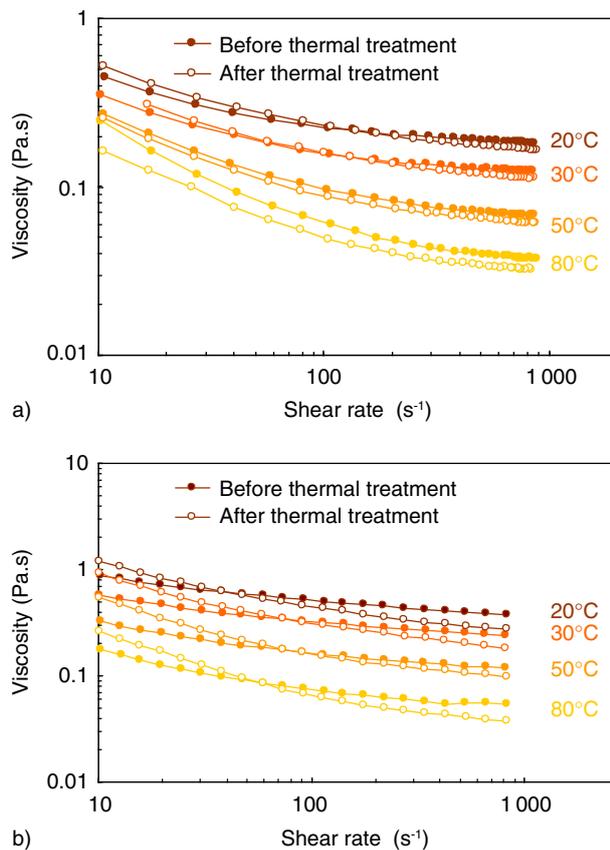


Figure 12

Flow curves of the HP-HT fluorinated mud a) Fomblin[®] Y04 and Fluorolink[®] F10 PFPE; b) Fomblin[®] 2045X-Fluorolink[®] F10 PFPE before and after thermal treatment at 250°C for 24 hours.

3.4.1 Resistance to Hydrocarbons Influx

The resistance to hydrocarbon influxes has been evaluated by introducing into the fluorinated mud (Y04-F10) two different light oil cuts: a naphtha (saturated) and a kerosene (aromatic). Mixing was applied with the Ultra Turrax[®] T25 homogeniser, set at 11 000 rpm for 5 minutes. The mixture is composed of 10 mL of mud and 10 mL of cut. The response of the mud against naphtha and kerosene is exactly the same: as soon as the stirring is stopped, the two phases quickly separate with the mud going down and the cut going up. Both phases have been analyzed to check if they had been contaminated during mixing:

- an IR spectrum was performed on the supernatant (cut);
- a DSC and IR analysis were carried out on the bottom (mud).

On the IR spectra of kerosene and naphtha after contact with the mud no fingerprints of O-H and C-F bonds could be identified demonstrating that the cut does not contain any water nor PFPE polymer from the mud. As an example in Figure 15 IR spectrum of kerosene after contact is reported.

The DSC analysis that was carried out on the mud after mixing with kerosene or naphtha shows that water droplets are still dispersed in the mud. Crystallization peaks below -20°C were obtained, meaning that no coalescence took place and that the droplet diameter is still sub micronic. This result confirms the stability of the emulsion.

The results of IR spectra on the mud (Fomblin[®] Y04 and Fluorolink[®] F10 PFPE) after mixing with kerosene or naphtha do not reveal any C-H fingerprint showing that the mud does not retain hydrocarbons from the cut.

3.4.2 Resistance to Gas Influx

In case of a kick with hydrocarbon gases, the mixture between mud and influx can lead to very complex and multiphase flow. Actually, temperature and pressure will govern the thermodynamic equilibrium between dissolved and free gas. Below the bubble point, gas bubbles can expand and lead to violent flashing. The foamy behaviour of the fluorinated mud (Fomblin[®] Y04 and Fluorolink[®] F10 PFPE) has been studied in the pressure cell of the controlled stress rheometer AR2000 from TA Instruments.

The test comprises two successive steps:

1. the first step consists of dissolving methane in the sample under sufficient pressure (1 000 psi) and enough shearing (500 s^{-1}). This step is maintained until the system reaches the equilibrium prevailed by Henry's law *i.e.* saturation;
2. during the second step, the system is suddenly depressurized from the applied saturation pressure (1 000 psi) to atmospheric pressure, while viscosity is continuously measured.

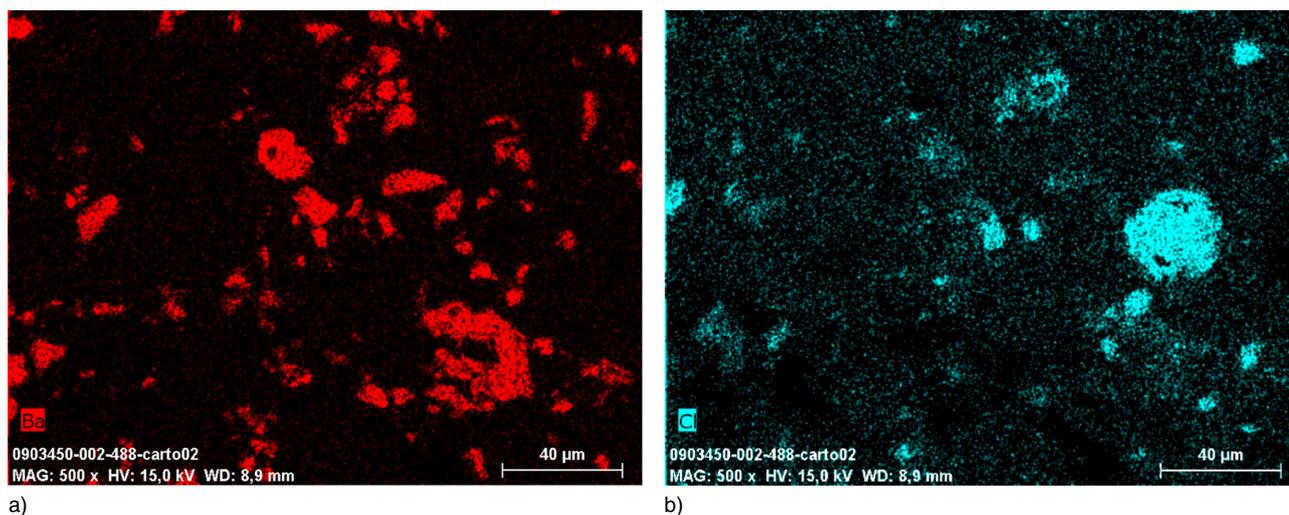


Figure 13

Cryo-SEM elemental analysis of the HP-HT fluorinated mud; a) barium; b) chlorine.

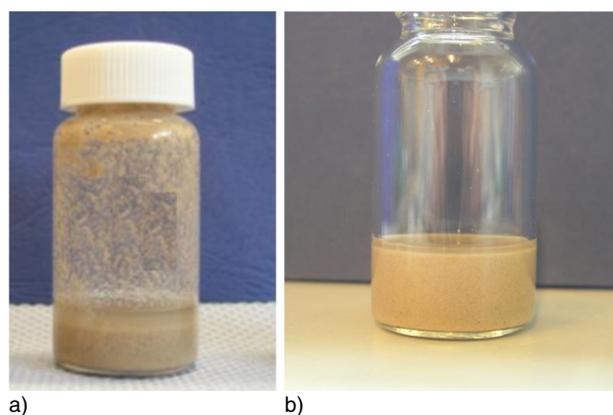


Figure 14

HP-HT Fluorinated muds after having been exposed to 300°C during 24 hours; a) Fomblin® Y04 and Fluorolink® F10 PFPE; b) mud Fomblin® 2045X-Fluorolink® F10 PFPE.

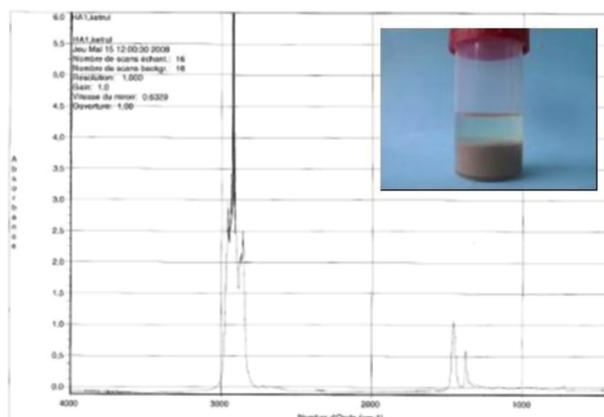


Figure 15

HP-HT Fluorinated muds after having been exposed to 300°C during 24 hours; a) Fomblin® Y04 and Fluorolink® F10 PFPE; b) mud Fomblin® 2045X-Fluorolink® F10 PFPE.

During these two steps, temperature is set at 20°C.

A viscosity decrease is observed, due to the solubility of methane under pressure, the methane acting as a diluent. When pressure is returned to atmosphere, bubbles of methane appear, expand and escape from the mud. As methane is released, dilution is no longer effective and viscosity increases and goes back to its initial value. This result demonstrates that the fluorinated mud does not retain the gas as a bubbly liquid (Fig. 16). It let it gently escape with no violent flashing or overshoot of viscosity, which is quite an advantageous property in case of gases influxes.

3.4.3 Resistance to Water Influx

Water intrusion may also be encountered while drilling and may contaminate the mud. To determine its effect, salted water and the fluorinated mud (Fomblin® Y04 and Fluorolink® F10 PFPE) have been mixed with a Ultra Turrax® T25 homogeniser at 11 000 rpm during 5 minutes. A volume of 10 mL of salted water was introduced in 10 mL of PFPE mud. Two salinities have been tested: 15 and 150 g/L of CaCl₂. In each case, the two phases instantaneously separate with the water going up and the mud going down. After mixing, a DSC analysis was performed on the mud. On the

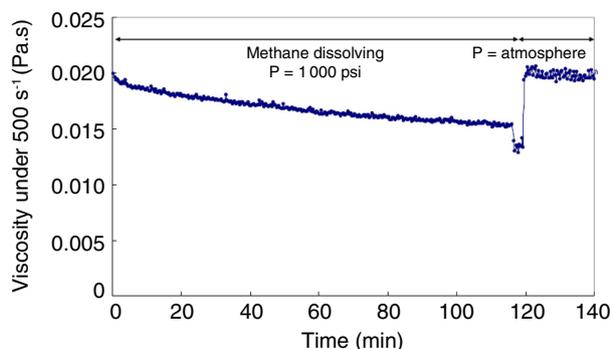


Figure 16

Foamy behaviour of fluorinated mud (Fomblin® Y04 and Fluorolink® F10 PFPE) with methane.

resulting thermographs crystallization were observed, demonstrating that the mud still contains emulsified water. During the mixing, the water droplets did not escape from the mud to the free aqueous phase.

CONCLUSIONS

PFPE muds appear as a real breakthrough for HP-HT drilling challenges. They meet the following specified requirements:

- limited amounts of weighting materials,
- versatility of density,
- immiscibility with reservoir fluids (water, gas, hydrocarbons),
- low viscosity,
- excellent thermal stability (up to 300°C),
- environmentally safe,
- easy to formulate.

Fomblin® Y PFPE and Fluorolink® F10 PFPE have been registered by CEFAS (Centre for Environment Fisheries and Aquaculture Science) in the UK. They have been classified using test protocols approved by OSPAR with the Offshore Chemicals Notification Scheme (OCNS). Both products were ranked into the group D under the Non-Charm classification model, A representing the highest environmental hazard and E the lowest.

To our knowledge, none of the known drilling fluids (OBM, WBM, formate brines) can achieve such properties.

Significant challenges remain to face. Actually, due to the particular composition of the fluorinated muds, conventional drilling fluid additives are not efficient. For example, the developed muds show excessive fluid loss. There is thus a need to develop new chemistries for additives, compatible with PFPE, such as new filtration control agents. Successful tests have been

obtained recently with PFPE particles [40]. The further study of the structure-property relationships could help to optimize formulations. As PFPE can be quite easily functionalized and tailored for given applications, we are confident with the future development of such fluorinated muds.

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