AADE-10-DF-HO-37

Environmentally Responsible Water-Based Drilling Fluid for HTHP Applications

Jorge M. Fernandez and Steve Young, M-I SWACO

Abstract

This paper describes the development of a new chrome-free, high-temperature, high-pressure (HTHP) stable water-based fluid system. The new fluid uses a combination of clay and unique chrome-free additives that provide exceptional fluid-loss control and rheological stability to temperatures exceeding 400°F (204°C), and at densities exceeding 18 lb/gal. The paper presents the results of extensive development testing demonstrating the flexibility of the new fluid and its tolerance to drill solids contamination. Results from some initial field testing of the fluid system are also presented.

Industry economics, coupled with stricter environmental regulations, have provided the impetus for the increased use of water-based drilling fluids with the capacity to operate similarly to invert emulsion drilling fluids in HTHP conditions. Chrome-containing materials were, and in many places still are, commonly part of these high-temperature water-based fluids, acting as efficient, stable dispersants and fluid-loss control agents. The tightening of environmental discharge regulations has placed restrictions on the use of chrome-based products in water-based fluids and as such, alternative, chrome-free, HTHP drilling fluids are required that will demonstrate an equivalent or improved performance to the current chrome-containing high-temperature, high-density water-based fluid systems. Under high temperature conditions, the thermal degradation of polymers that control fluid loss and rheological properties create major challenges for fluid performance and stability. Additionally, the gelation of water-based fluids containing clays and/or drill solids can become difficult to control under high temperature conditions. Both of these issues are compounded when the high temperature is coupled with a requirement for high fluid density.

Introduction

Environmental and economical considerations have led to increasing use of water-based drilling fluids (WBM) in applications where oil-based drilling fluids (OBM) have previously been preferred, including high-temperature, high-pressure (HTHP) wells. In an increasing number of areas in the world environmental regulations prohibit the discharge of oil-based mud and cuttings containing OBM. These HTHP wells, can be defined as those with a bottomhole temperature between 300° and 500°F and an expected shut-in pressure from 10,000 to 25,000 psi. Conn *et al*. (2004). Dispersed WBM are among the most popular drilling fluids thanks in part to their reputation as easy to maintain, economically competitive drilling fluids. Such fluids can be designed and engineered to be suitable for HTHP environments.

A typical dispersed WBM contains water, bentonite and a myriad of additional components to control fluid loss and provide rheological stability. In high-temperature applications, WBM require bentonite stabilizers (thinners) to keep the clay from flocculating in order to maintain favorable rheological and fluid-loss characteristics. To improve the rheological stability and fluid-loss properties of these fluids at elevated temperatures, chromium-containing thinners and fluid-loss additives have been successfully applied.

Early dispersed water-based fluid designs involving the use of thinners such as sodium chloride, sodium tetraphosphate, and quebracho were sufficient for the conditions of these early wells, however those components no longer provide the performance necessary for today's wells that are drilled under HTHP conditions. Thinners that provided the necessary technical performance such as chrome lignosulfonates or chrome lignites have not been permissible in many areas for a number of years because of environmental regulations restricting chrome use and discharge. There is an increasing need for an efficient chrome-free drilling fluid system with cost and performance characteristics similar to those of chromium-based systems.

Ibrahim *et al.* (2003) described the primary mechanism of action for deflocculants as preventing clay platelets from bonding together by satisfying the clay plate edge charges and eliminating the electrochemical attractive forces between clay particles. Lignosulfonates and lignites themselves are relatively efficient in performing this function, but adsorption onto the clay edge is enhanced through the inclusion of multi-valent metals such as chrome. Chrome lignosulfonates in addition to acting as very efficient thinners also impart excellent fluid loss properties to the fluid and provide good wellbore stability by stabilizing the reactive shales.

One alternative to chrome has been to manufacture lignosulfonate additives complexed with other metal ions, *e.g.*, Fe, Ti and Zr. Park (1988) reported that the mixed titanium/zirconium lignosulfonate salt is very effective for controlling rheology and preventing progressive gel structure at elevated temperatures. Others (Burrafato *et al.* 1995; Miano *et al.* 1996; Nicora & Burrafato, 1998) investigated the use of zirconium citrate as a substitute for chromium lignosulfonate and reported its effectiveness in controlling high-temperature gelation of dispersed WBM's at temperatures exceeding 400°F (204°C). These solutions have not proven to be as effective as chromium lignosulfonate when tested in a wide range of applications.

An efficient chemical alternative to metal complexed lignites or lignosulfonates involves the use of synthetic polymers that can function at high temperatures and are resistant to various contaminants. These low-molecular weight anionic polymers function in much the same chemical way as lignosulfonates, by neutralizing the positive charges on the clay edges and thus preventing flocculation. Low-molecular weight anionic polymers have been successfully used for a number of years as mud conditioners to stabilize the clay-based rheological profile before and after aging as was demonstrated by Chesser *et al.* (1979).

Another group of synthetic materials that have been available for use as higher temperature stable rheological and fluid-loss control additives for many years are sulfonated polymers, copolymers and terpolymers. Compared to biopolymers and starches, such synthetic polymers exhibit a much greater thermal stability and can also exhibit a greater resistance to solids and other contaminants. Among the most significant chemistries that have been designed to challenge chrome-free additives for water-based fluids, is the development of synthetic polymers that control fluid loss without any significant impact on rheology.

An alternative is still needed that is resistant to various contaminants, controls rheology, and is stable at high temperatures (without causing gelation or a progressive gel structure). The use of a single product to replace chrome-based conditioners, although ideal, has so far not been achieved. Through the use of a combination of chrome-free additives, it has been possible to equal the performance of WBM with chrome-based products. This paper describes the development of a new low-colloid, chrome-free, high-density HTHP water-based drilling fluid that uses a combination of select clay and synthetic polymers to provide excellent fluid-loss control and to generate a thermally stable rheology equaling that of a chrome-containing WBM. This paper presents a culmination summary of the results from extensive testing that demonstrates the optimal combination of chemistries that are needed to perform like a well designed dispersed water-based mud with chrome additives. Also highlighted are results from initial field testing of the fluid system.

High-Temperature Fluid Loss Additives

The early successful utilization of high-molecular weight polymers includes applying vinyl sulfonate copolymers in geothermal drilling applications during the mid-1980's. Perricone *et al.* (1986) described the properties of high-molecular-weight vinyl sulfonate copolymers as high temperature fluid-loss control additives in WBM at temperatures of 350°F (177°C). Thaemlitz, *et al.* (1999) described a high-temperature filtration control additive for WBM which was a cross-linked copolymer of acrylamide and a sulfonated monomer. The cross-linked copolymer was shown to provide effective filtration control and to retain stability at temperatures up to 450°F (232°C).

The most prevalent synthetic polymers for high-temperature WBM have been copolymers based on acrylamide and sulfonated monomers as depicted in Figure 1. The majority of synthetic polymers that were evaluated during the extensive development work that led up to this paper were based on similar types of monomers. Some of the products evaluated were cross-linked to varying extents in an effort to control the rigidity of the copolymer in order to achieve a desirable balance between fluid-loss and rheology control in the drilling fluid. According to the observations made by Thaemlitz *et al.* (1999), the degree of crosslinking plays an important role in copolymer solubility, which is related to the ability to control fluid loss. Too much crosslinking will result in a polymer that has a very rigid structure and can be difficult to hydrate in water-based fluids. A low degree of crosslinking produces polymers that hydrate rapidly and may cause too much rheology. In addition such polymers are known to have limited tolerances to contamination and shear.

Another group of products, which were formulated as being non-crosslinked, utilized a controlled molecular weight and carefully chosen degree of substitution and functionality of the polymer to control both its structural rigidity and temperature tolerance. Indeed, Wilcox *et al.* (1988) note that the inherent polymer properties of molecular weight and charge density can be used to dictate the function of the polymer as a flocculant, deflocculant, or a fluid-loss additive.

Laboratory WBM Development

Following on from the work conducted by Tehrani *et al.* (2009), an extensive laboratory evaluation of both fluid-loss control polymers and thinners/deflocculants was conducted on a 15.0-lb/gal formulation dynamically aged at 482°F (250°C). This temperature represented the upper limit of what could safely be tested with generally available laboratory equipment without resorting to the use of specialized equipment. The base fluid utilized was based on freshwater, selected clay, API barite and additives to help control rheology, fluid loss control and also to provide temperature stability. Initial work commenced with the use of sepiolite clay instead of the traditional Wyoming bentonite with the supposition that the 482°F (250°C) aging temperature would exceed the capabilities of the bentonite clay to provide an acceptable base for filtration and rheology. Much of the work cited by Zilch *et al.* (1991) in the development of geothermal drilling fluids demonstrated that rheological stability and filtration control could be maintained with bentonite-based fluids using ferrochrome lignosulfonate at 350°F (177°C) with serious decomposition and fluid flocculation occurring at 450°F (232°C).

A favorable formulation was first established with the use of chrome lignite in order to establish a benchmark for comparison of all subsequent formulations featuring chrome-free deflocculants. Mixing and addition conditions were established and controlled to both optimize additive performance and to ensure a good comparison between formulations. All fluids were initially mixed with dry sodium hydroxide added to the water and clay in order to establish full yield of the clay. Before aging, but after initial rheological properties were recorded, an oxygen scavenger was added to the fluid and the aging cells utilized were thoroughly purged with nitrogen to mitigate any thermal oxidative decomposition of the additives. After dynamically aging for a standard 16 hours the fluids were re-homogenized and the pH was adjusted to 10 with a 50% sodium hydroxide solution.

After establishing a chrome-based formulation with the most competitive blend of fluid loss polymers, work continued on substituting chrome materials with combinations of modified lignitic and lignosulfonate based materials in addition to using low-molecular weight, thermally stable, anionic polymers. Once the optimal chrome-free thinner combinations and concentrations were established, the formulation was tested with bentonite clay in place of sepiolite to determine the efficacy of the chrome-free additives in a much more challenging environment. A stress study was completed on the bentonite-based fluids by increasing the weight of the formulation from 15 to 17.0 lb/gal with only the addition of barite. As an additional test, performance was also evaluated with the addition of synthetic seawater.

The general specifications that were set to define the performance of the ideal fluid included a Plastic Viscosity (PV) of less than 30 cP, a 6-rpm reading between 7 and 10, and HTHP fluid-loss filtrate of less than 30 mL at 300°F (149°C), and 500-psi differential pressure on hardened paper. The rheological properties were measured at 150°F (66°C). API low-temperature/low-pressure fluid loss as described in API Recommended Practice 13B-1 was used as a screening tool to determine which fluids would be selected for fluid-loss evaluation under HTHP test conditions. An API fluid loss of <6 mL after dynamic aging was considered suitable for testing.

Laboratory WBM Results

Table 1 shows a selection of the different formulations tested with sepiolite as the base clay while varying different thinners and thinner combinations. The benchmark formulation was established with chrome-lignite and a combination of synthetic polymers for optimum fluid loss and rheology control.

Of the six deflocculant variables tested, one, a zirconium complex blend (Fluid #2), demonstrated a truly unacceptable rheological profile indicating flocculation, with the zirconium salt itself (Fluid #6) showing a similar type of response. Two of the deflocculant combinations - Fluid #3, a mixed metal lignosulfonate, and Fluid #5, a divalent metal lignosulfonate, came close to the baseline rheological profile, including gel strengths, obtained with the chrome-lignite as can be seen in Table 2. The API fluid loss test, however, demonstrated that the chrome-free fluids did not perform as well as the chrome containing fluid in providing the desired level of fluid loss control.

Table 3 illustrates the formulations tested with the best two chrome-free lignosulfonate performers using bentonite as the base clay and stressing these formulations by the addition of 11.5 vol% of synthetic seawater and also an additional 140 lb/bbl of weighting material. The concentrations of lignosulfonate blends and low-molecular-weight anionic polymers were maintained the same as in the testing with sepiolite as the base clay. In this more challenging environment, the divalent metal lignosulfonate and low-molecular-weight anionic polymer combination demonstrated remarkable performance in its ability to maintain a stable rheological profile and HTHP fluid-loss control after aging as demonstrated in Table 4. Additionally, the divalent metal lignosulfonate/low-molecular-weight anionic polymer deflocculant combination performed well under the two stress tests.

Based on these results, and earlier work, a selection of optimal products was made that will allow a chrome-free WBM to be readily formulated and engineered to perform in a similar manner to the best chrome-containing HTHP WBM.

Field Application – Southeastern Hungary

The first field application of this chrome-free WBM in south eastern Hungary involved drilling in a shale gas reservoir. In this sensitive area the primary environmental concern with WBM was to minimizing the use and discharge of heavy metals such as chrome. For this field test case the HPHT WBM was required to exhibit stability of properties at a 16.7-lb/gal density at a temperature of 400°F (204°C), and also have the capability for the density to be increased by 2.5 lb/gal to 19.2 lb/gal (preferably with the weighting agent addition as the only treatment) without significantly affecting rheology.

A series of laboratory tests were undertaken to fine-tune the fluid formulation to achieve the desired performance characteristics. The final optimized formulation tested is outlined in Table 5, with the results obtained from this testing being shown in Table 6.

The field mud used was based on the formulation recommended in Table 5. The fluid was readily mixed at the rigsite and was displaced into the well at 2730-m depth. Drilling progressed with no major incidents to 3130 m where a casing was set, then the well was drilled to TD at 3680 m, where the final mud weight was 17.5 lb/gal. Figure 2 and Figure 3 show a graphical plot of the main drilling fluid rheological and fluid loss properties against depth. This field data shows the property control and stability that was achieved with this chrome-free HTHP WBM. The “blip” in properties at 3130 m can be attributed to cement contamination in the sample tested.

Conclusions

A combination of bentonite clay and specific high-molecular-weight synthetic polymers provided good fluid-loss control while maintaining an adequate initial rheological profile and rheological stability after aging.

Although plastic viscosity (PV) and low-end rheology are good indicators of flocculation, the gel strengths provide an additional method to differentiate the deflocculant additives.

Many of the fluids tested demonstrated very positive rheological profiles but produced unacceptably high gel strengths. The rheological profile and gel strengths can be managed through the proper selection of clays and balancing the ability of the fluid to provide good fluid loss control and a shear thinning rheological profile with significant gel strength.

A combination of a divalent metal lignosulfonate and low-molecular-weight anionic polymer produced the synergism necessary to provide a stable rheology and fluid loss both before and after aging at 482°F (250°C).

The first field trials of this chrome-free HTHP WBM have proven to be very successful, with field performance reflecting that seen during the design phase in the laboratory.

Acknowledgments

The authors would like to thank Ahmadi Tehrani and Donna Gerard for their exhaustive research and also M-I SWACO for supporting this research and for allowing us to publish this report.

References

1. Park, L.S. "A New Chrome-Free Lignosulfonate Thinner: Performance Without Environmental Concerns." SPE 16281, SPE International Symposium on Oilfield chemistry, San Antonio, Texas, February 4-6, 1987 and *SPE Drilling Engineering* (September 1988) 311-314.
2. Burrafato, G., Miano, F., Carminati, S. and Lockhart, T.P. "New Chemistry for Chromium-Free Bentonite Drilling Fluids Stable at High Temperatures." SPE 28962, SPE International Symposium on Oilfield Chemistry, San Antonio, Texas, February 14-17, 1995.
3. Miano, F., Carminati, S., Lockhart, T.P. and Burrafato, G. "Zirconium Additives for High-Temperature Rheology Control of Dispersed Muds." SPE 28305, *SPE Drilling & Completion*, vol.11, no.3 (September 1996) 147-152.
4. Nicora, L.F. and Burrafato, G. "Zirconium Citrate: A New Generation Dispersant for Environmentally Friendly Drilling Fluids." SPE 47832, IADC/SPE Asia Pacific Drilling Technology Conference, Jakarta, September 7-9, 1998.
5. Chesser, B.G. and Enright, D.P. "High Temperature Stabalization of Drilling Fluids with a Low Molecular Weight Copolymer." SPE 8224, SPE Annual Fall Technical Conference, Las Vegas, Nevada, September 1979.
6. Perrocine, A.C., Enright, D.P. and Lucas, J.M. "Vinyl Sulfonate Copolymers for High-temperature Filtration Control of Water-Based Muds." SPE 13455, *SPE Drilling Engineering*, vol.1, no.5 (October 1986) 358-364.
7. Thaemlitz, C.J., Patel, A.D., Coffin, G. and Conn, L. "New Environmentally Safe High-Temperature Water-Based Drilling-Fluid System." SPE 37606, SPE/IADC Drilling Conference, Amsterdam, March 4-6, 1997 and *SPE Drilling & Completion*, vol.14, no.3 (September 1999) 185-189.
8. Conn, L. and Roy, S. "Fluid Monitoring Services Raises Bar in HTHP Wells." *Drilling Contractor* (May/June 2004) 52-53.
9. Tehrani, A., Gerrard, D., Young, S., Fernandez, J., "Environmentally friendly water based fluid for HPHT drilling", SPE 121783, presented at SPE oilfield chemistry symposium, The woodlands, Texas, April 2009.
10. Ibrahim, M.N.M., Chuah, S.B. and Cheng, P.Y. "Tin-Tannin Lignosulfonate Complex: An Improved Lignosulfonate-Based Drilling Fluid Thinner." *Jurnal Teknologi* vol.38, no.F (June 2003) 25-32.
11. Wilcox, R.D. and Jarrett, M.A. "Polymer Deflocculants: Chemistry and Application." SPE 17201, IADC/SPE Drilling Conference, Dallas, February 28 - March 2, 1988.
12. Zilch, H.E., Otto, M.J. and Pyle, D.S. "The Evolution of Geothermal Drilling Fluid in the Imperial Valley." SPE 21786, SPE Western Regional Meeting, Long Beach, California, March 20-22, 1991.

Table 1 – WBM Formulations with Sepiolite as the Base Clay

Products (lb/bbl)	Base	Fluid 1	Fluid 2	Fluid 3	Fluid 4	Fluid 5	Fluid 6
Water	238	238	238	238	238	238	238
Sepiolite	8	8	8	8	8	8	8
Caustic Soda	2	2	2	2	2	2	2
AMPS copolymer	1	1	1	1	1	1	1
Acrylate copolymer	3	3	3	3	3	3	3
Low-molecular-weight anionic polymer	-	5	5	5	5	5	5
Chrome- lignite dispersant	15						
Polymer/mixed metal lignosulfonate blend		15					
Zirconium complex/polymer blend			15				
Mixed metal lignosulfonate				15			
Metal lignosulfonate					15		
Divalent metal lignosulfonate						15	
Zirconium complex							15
Resinated lignite complex	6	6	6	6	6	6	6
Polyglycol/gilsonite blend	18.4	18.4	18.4	18.4	18.4	18.4	18.4
Barite	296	296	296	296	296	296	296
Oxygen Scavenger	2	2	2	2	2	2	2

Table 2 – WBM Results for Sepiolite as Base Clay Formulation

Fluid Properties*	Base	Fluid 1	Fluid 2	Fluid 3	Fluid 4	Fluid 5	Fluid 6
600-rpm reading	51	54	90	55	66	43	69
300-rpm reading	30	39	69	38	44	24	57
200-rpm reading	23	33	60	32	37	19	54
100-rpm reading	15	27	48	24	28	12	48
6-rpm reading	7	20	35	14	16	4	56
3-rpm reading	6	18	34	13	15	3	53
PV (cP)	21	15	21	17	22	19	12
YP (lb/100 ft^2)	9	24	48	21	22	5	45
10-sec Gel(lb/100 ft^2)	10	26	45	20	27	5	61
10-min Gel (lb/100 ft^2)	28	45	97	36	59	25	72
API Fluid Loss (mL/30 min.)	4.5	21	7.5	10.5	14.5	8	8.5

*Fluid properties after aging at 482°F(250°C) for 16 hours. Rheological properties recorded at 150°F(66°C).

Table 3 - WBM Formulation with Bentonite as the Base Clay

Products (lb/bbl)	Base	Base a	Base b	Fluid 3	Fluid 3a	Fluid 3b	Fluid 5	Fluid 5a	Fluid 5b
Water	238	238	238	238	238	238	238	238	238
Sepiolite	8	8	8	8	8	8	8	8	8
Caustic Soda	2	2	2	2	2	2	2	2	2
AMPS copolymer	1	1	1	1	1	1	1	1	1
Acrylate copolymer	3	3	3	3	3	3	3	3	3
Low-molecular-weight anionic polymer	-	-	-	5	5	5	5	5	5
Chrome-lignite dispersant	15	15	15						
Mixed metal lignosulfonate				15	15	15			
Divalent metal lignosulfonate							15	15	15
Resinated lignite complex	6	6	6	6	6	6	6	6	6
Polyglycol/gilsonite blend	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4
Barite	296	456	296	296	456	296	296	456	296
Synthetic seawater	-	-	41	-	-	41	-	-	41
Oxygen Scavenger	2	2	2	2	2	2	2	2	2

Table 4 – WBM Results for Bentonite as Base Clay Formulation

Fluid Properties*	Base	Base a	Base b	Fluid 3	Fluid 3a	Fluid 3b	Fluid 5	Fluid 5a	Fluid 5b
600-rpm reading	76	107	55	108	182	80	51	67	40
300-rpm reading	46	71	35	75	138	58	30	49	24
200-rpm reading	36	61	27	65	112	49	20	38	18
100-rpm reading	24	43	19	51	90	40	15	32	12
6-rpm reading	9	18	9	31	65	25	8	21	7
3-rpm reading	8	16	8	29	64	24	6	20	5
PV (cP)	30	36	20	33	44	22	21	18	16
YP (lb/100 ft^2)	16	1635	15	42	94	36	9	31	8
10-sec Gel (lb/100 ft^2)	15	35	15	35	67	30	13	37	5
10-min Gel (lb/100 ft^2)	43	80	29	48	107	47	42	65	12
API Fluid Loss (mL/30 min.)	4.9	5.6	7.9	9.5	12	13.5	5	4	7.5
HTHP Fluid Loss (mL/30 min.)	19.8	27.2	32.4	-	-	-	20	25.2	31

*Fluid properties after aging at 482°F (250°C) for 16 hours. Rheological properties recorded at 150°F (66°C).

Table 5 –WBM Formulation for Southeastern Hungary

Products (lb/bbl)	16.7 lb/gal	19.2 lb/gal
Water	222	189
Soda Ash	0.25	0.25
Caustic soda	2	2
Gel Supreme	3	3
Acrylamide terpolymer	2	2
Nano-latex copolymer	10	10
Rheological modifier	2	2
Dispersant	15	15
Resinated lignite	3	3
Oxygen Scavenger	2	2
Barite	443	581

Table 6 –WBM Results for Southeastern Hungary

Fluid Properties	Units	T (°F)	16.7 lb/gal	19.2 lb/gal
600-rpm reading	lb/100 ft^2	120	60	94
300-rpm reading	""	“”	33	58
200-rpm reading	""	“”	24	46
100-rpm reading	""	“”	15	33
6-rpm reading	""	“”	4	18
3-rpm reading	""	“”	3	18
PV	cP	“”	27	36
YP	lb/100 ft^2	“”	6	22
10-sec Gel	""	“”	4	18
10-min Gel	""	“”	14	32
HTHP	mL/30 min	300	17.8	12.0

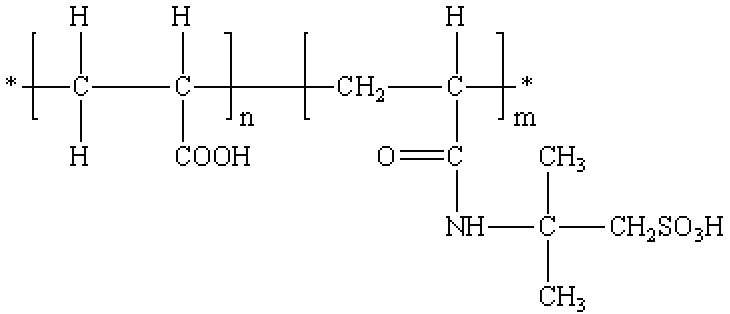


Figure 1 – General AA/AMPS Copolymer

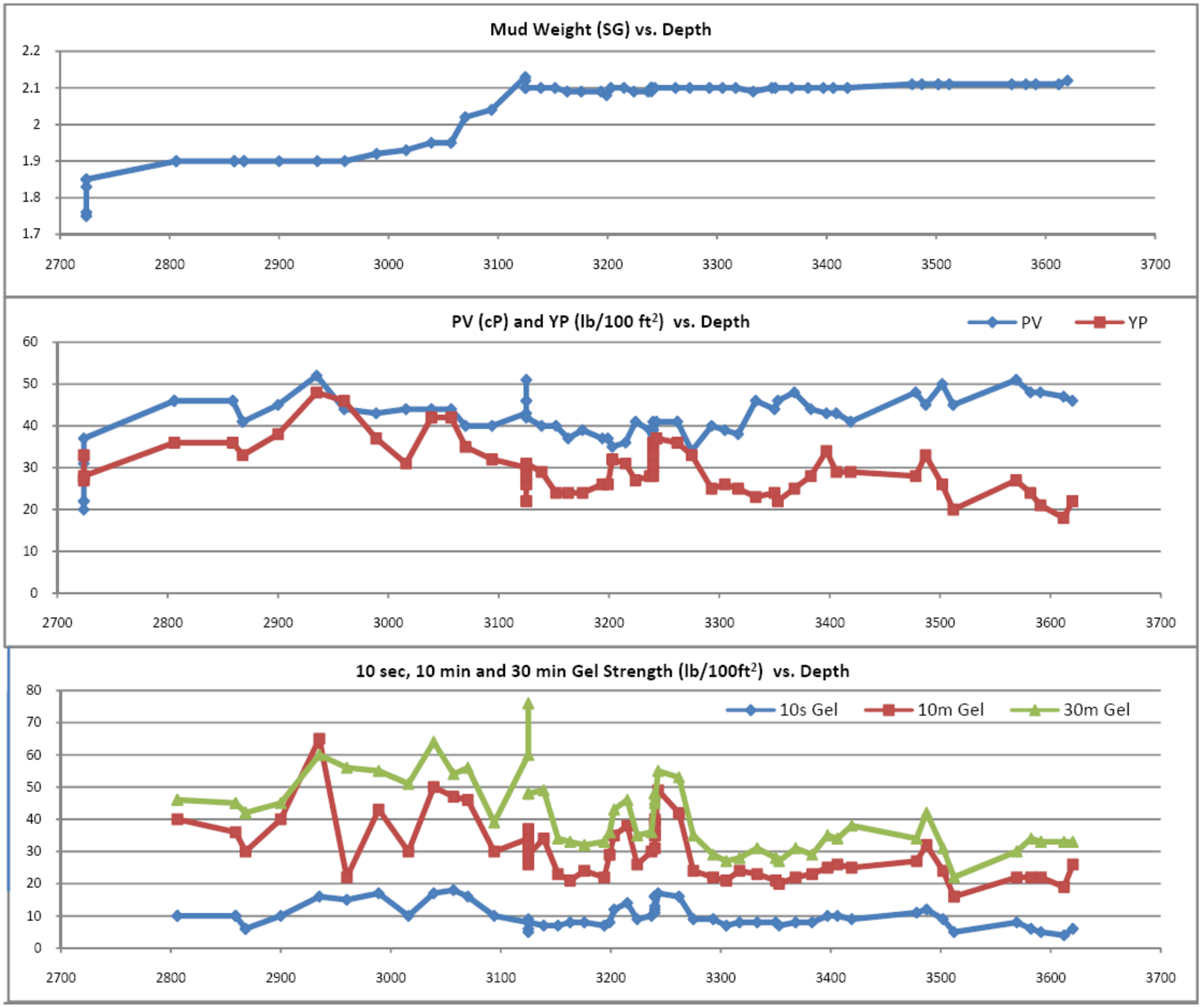
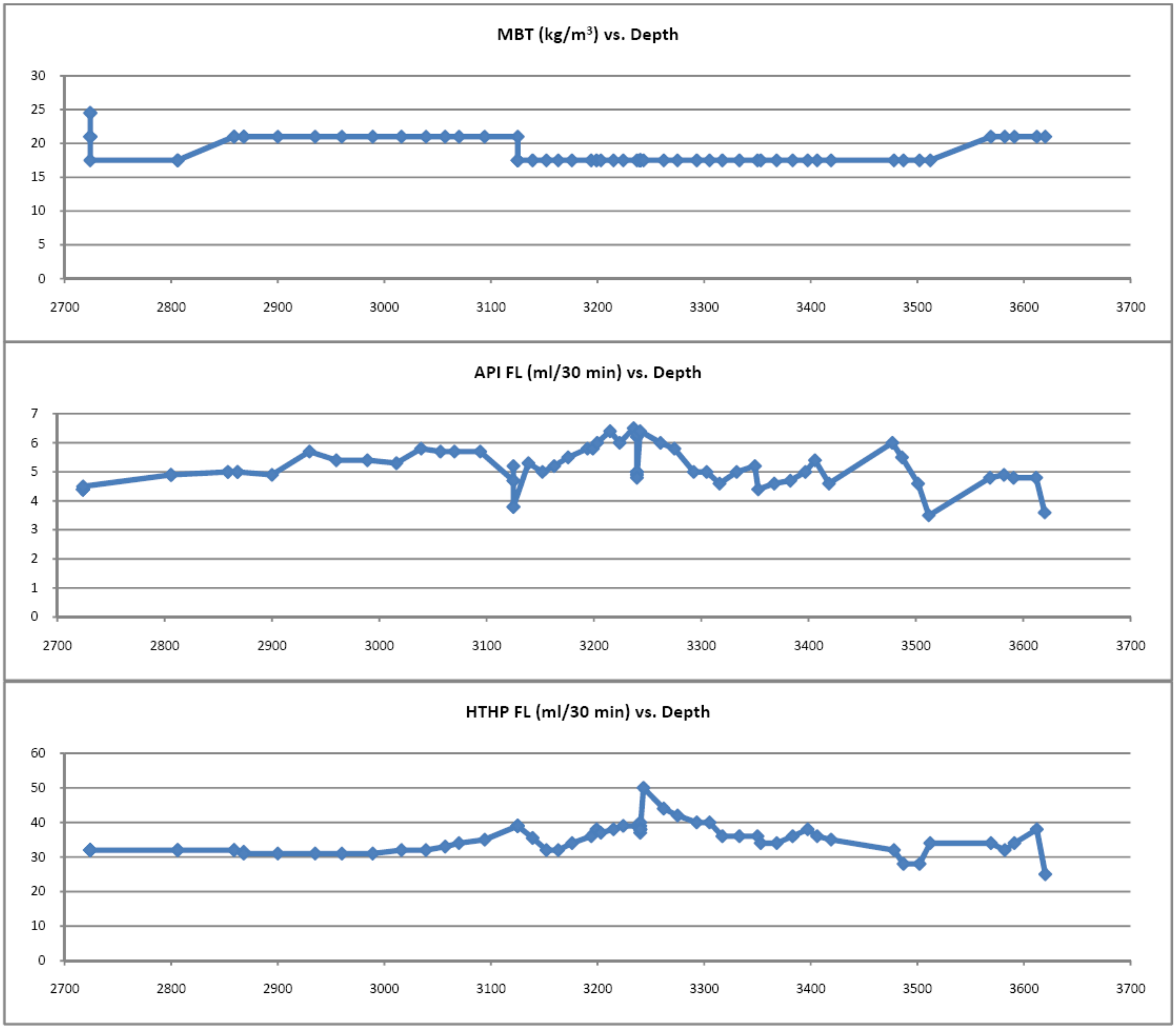


Figure 2 – Rheological profile from field data for formulation used in Hungary.



MBT (kg/m^3) vs. Depth

API FL (ml/30 min) vs. Depth

HTHP FL (ml/30 min) vs. Depth

Figure 3 - MBT and Fluid Loss data from field data for formulation used in Hungary.