



Invert Emulsion Fluid System with Enhanced Rate of Biodegradation

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This paper was prepared for presentation at the AADE 2002 Technology Conference "Drilling & Completion Fluids and Waste Management", held at the Radisson Astrodome Houston, Texas, April 2 – 3 2002 in Houston, Texas. This conference was hosted by the Houston Chapter of the American Association of Drilling Engineers. The information presented in this paper does not reflect any position, claim or endorsement made or implied by the American Association of Drilling Engineers, their officers or members. Questions concerning the content of this paper should be directed to the individuals listed as author/s of this work.

Abstract

In the last few years, regulations to minimize environmental impact from drilling operations have led the industry to generate several environmentally friendly synthetic based drilling fluids. Base fluid toxicity and their chemical biodegradation in a marine environment are important parameters in assessing the impact of discharging fluids used on offshore drilling operations. Discharge of cuttings at sea is being evaluated around the world, to further protect the marine environment. Increasingly, cuttings are shipped onshore and processed or re-injected. In both cases, it burdens the cost of the drilling operations, and still may have a negative impact on the environment. This paper will discuss a newly developed and optimized process to enhance the rate of biodegradation of currently used mineral, synthetic or ester based fluids. The process consists of using a treatment comprising organic nitrogen and phosphorus compounds combined with fatty acids which are added to a typical synthetic-based drilling fluid. Extensive laboratory work and research have been conducted. Results indicate this non-toxic and more readily biodegradable approach will have a greater reduced impact on the environment than the currently available synthetic fluids.

Introduction

In the past few years discharge restrictions of oil base mud cuttings into the sea and other environmentally sensitive areas, lead to the development of synthetic-based fluids. To offset the high cost of cutting injection, shipment and treatment, the search for a greener, more economical drilling fluid became apparent and continues today. This paper focuses on a more readily biodegradable drilling fluid approach, which maintains the high performance of standard synthetic-based fluids. Previous laboratory work conducted by the authors indicated that the rate of biodegradation of synthetic and mineral base fluids could be enhanced by incorporation a special additive to the drilling fluid system. This special additive is referred to as booster fluid in this paper. Refer to SPE paper 61212 for previous investigation and findings. Extensive laboratory testing was conducted and the resulting obtained data confirmed the ecological importance of this novel drilling fluid. Mineral oil, linear alpha olefins (LAO), isomerized olefins (IO) and ester

base fluids behave differently. Their toxicity and biodegradation properties can vary widely. A major hurdle in this study was to find a compromise between toxicity and biodegradation rate while, maintaining adequate fluid properties. The booster fluid can be added to synthetic IO, LAO, paraffin, mineral oil or ester base invert fluid. Because of its high performance characteristics, thorough lab testing was conducted on IO base fluid. Stable drilling fluid with low yield point and adequate 6 and 3 rpm Fann 35 readings, result in the IO system's hole cleaning and barite suspension. This system is applicable for deep water drilling and difficult HPHT wells. While the coming introduction of new EPA regulations may result in making this process unnecessary to meet new guidelines, the work is encouraging since it appears fluids can be boosted to degrade more effectively.

Previous work

Initial toxicity and biodegradation work was conducted on a booster component comprised of three additives including an acid, a nitrogen source and a phosphorus source. In this paper these booster additives will be referred to as Fatty acid, Nitrogen and Phosphorus respectively. Test results indicated that a synthetic fluid treated with this booster fluid biodegraded aerobically faster than the base fluid alone. Unfortunately, it exhibited a level of toxicity not passing the minimum acceptable EPA levels using the Gulf of Mexico protocol. Table 1 lists booster fluid composition and corresponding fluid properties. The rates of biodegradation and toxicity values are presented in Table 2 and Figure 2. The LC50 range finder tests were conducted on emulsion fluids treated with the booster fluid to evaluate the toxicity level. The positive increases in biodegradation combined with the less than desirable toxicity results on the initial work directed the team to an optimization process.

Optimization

The major part of the optimization process was devoted to the booster fluid to ensure that it is both non-toxic and more biodegradable than a regular synthetic fluid. The booster fluid in this optimization still consists of three key components, a phosphorous compound, organic nitrogen and a fatty acid source. The optimization testing included evaluation of three other products to provide

phosphorus. These phosphorus source products are referred to in this paper as Phosphorus 1, 2 and 3. Three booster fluids made with different phosphorus were formulated. The final corresponding products were each added to invert emulsion drilling fluid. Laboratory testing indicated that all three components had varying degrees of toxicity and had different effects on the fluids rheological properties and emulsion (Table 3). To achieve the highest rate of biodegradation it was necessary to go through a screening process to determine the optimum concentration of each component of the booster fluid. Based on results only the Phosphorus 3, exhibited lower toxicity level and a stable drilling fluid. This source was selected as the primary component of the booster fluid. A *Mysidopsis bahia* LC 50 range finder value of 54,700 ppm was obtained with the Phosphorus 3 treated drilling fluid. The next step was to evaluate the rate of biodegradability of the least toxic booster fluid. Aerobic biodegradation tests were conducted on several booster formulations using the Phosphorus 3 as a source of phosphorus, while maintaining the fatty acid and the nitrogen source. The booster fluid concentration added to an invert fluid is generally around 5 - 10% by volume of final barrel of mud, depending upon the type of the base oil.

Environmental impact

Marine toxicity tests

The toxicity effects of this biodegradable fluid and its impact on marine organisms were investigated. A 96 hour Range Finder was conducted on *Mysidopsis bahia* species and results indicated that the treated fluid had 54,700 ppm, exceeding the Gulf of Mexico minimum limit of 30,000 ppm suspended particulate phase (SPP) (Table 7). Sediment reworker test was also conducted on the crustacean, *Leptocheirus plumulosus*. Results show both fluids passing the 96 hours LC testing protocol.

Biodegradation tests

To assess the aerobic biodegradation we use an apparatus whose principle is based on the microorganisms' respiration (Figure 1). The samples to be tested are seeded with aerobic microorganisms in reactors. The oxygen is supplied by electrolysis of copper sulfate in an acid solution. The CO₂ resulting from biodegradation is absorbed by a lime solution. When bacteria consume O₂, a negative pressure in the testing reactor provides a supply of oxygen. The result of the test is presented in terms of milligrams of consumed oxygen. As reference an admitted biodegradable substance is used.

The next step was to target a drilling application of this novel fluid in the Gulf of Mexico. Several fluid formulations and biodegradation tests were conducted to

meet the current EPA regulations. At the time of testing the EPA regulations dictated that any new synthetic base fluid had to perform equal to or better than a C16-C18 isomerized olefin which in this paper is referred to as Standard base oil. For purpose of comparison, isomerized olefin (IO), synthetic paraffin (SP), refined paraffin (RP) and ester (E) base oils and corresponding invert mud was evaluated.

Aerobic biodegradation tests were conducted on base oils, corresponding invert drilling fluids with and without booster fluid. Results are presented in the form of oxygen consumption versus time in days. Data for base oils and muds are represented in Tables 4 and 5 and their oxygen consumption trends are shown in Figure 3 and 4. Complete data for fluid B with and without booster are not completely reported because the testing was in progress during the preparation of this manuscript. Overall these results clearly indicate the different rates of biodegradation of the base oils and muds. The positive aspect of this work is definite enhancement of the rate of biodegradation provided by this novel booster fluid additive.

Bioremediation tests

Biodegradation rate is an effective way to assess how fast micro-organisms can degrade a discharged base fluid, therefore permitting benthic fauna and marine life to re-colonize the cuttings piles.

Colonization experiments with autonomous landers were conducted on the deep sea floor at a depth of 1300 meters to evaluate the response of macrobenthos to various types of oil-based muds and cuttings. The purpose was to determine whether the macrobenthos behavior is caused by organic enrichment solely and/or is also influenced by other sources of stressors (e.g. toxicity). Three autonomous landers, each with 16 colonization trays, were deployed for period of 9 months. The trays were filled with an inert substance (glass beads) enriched with different type of organic substances (fish flour, oil bases muds and cuttings). Taxonomic composition and diversity indices of organically enriched and oil contaminated trays were fairly similar. These experimental results suggest that response to drilling fluids and cuttings contamination was mainly due to the organic enrichment rather than other sources of stress such as toxicity.

Results indicated that there was no damage to the deepwater marine organisms, supporting the novelty of this high performance additive to meet the environmental challenges facing drilling fluids in sensitive deepwater environments. Unfortunately data collected during the testing are still in progress and/or confidential and cannot be presented in this paper.

Laboratory evaluation

This new drilling fluid formulation and properties are similar to those of conventional synthetic fluids. The typical synthetic mud additives such as organo-clay, emulsifier, wetting agent, brine and weight material are all compatible. Figures 5 to 8 and Table 6. The only foreign additive needed to trigger the biodegradation process is the booster fluid. This new invert system is easy to maintain and is engineered the same as a standard synthetic drilling fluid.

Contamination testing and fluid stability

Evaluation of these new mud systems included the use of several laboratory methods to monitor behavior and fluid stability. They included resistance to contaminants, temperature and time stability. Also studied was the fluid effect on elastomers. Results of these tests show a stable fluid with good rheological properties can be formulated. See Table 6 for fluid properties after heat aging 16 hours at 150°C (300°F).

Return permeability tests conducted on Berea sandstone cores show that the system is non-damaging to production zones. This also indicates that even with the addition of booster fluid the drilling fluid system behaves as a conventional synthetic-based fluid.

Elastomers testing

Fluid samples were submitted for elastomers testing. Results of tests conducted on commonly used elastomers do not reveal any significantly detrimental effects. It is therefore concluded that this fluid is compatible with the particular elastomers tested. Test results are shown in Tables 8 and 9.

Benefits of the system

The tests also indicated that the addition of booster fluid would dramatically increase the biodegradability of the drilling fluid. This significantly reduces the environmental impact that results from the offshore dumping of drill cuttings generated with oil-base drilling fluids. This has a measurable impact on the cost and risk of offshore operations, and may eliminate the need to transport drill cuttings to shore bases for disposal in the future.

Field application

The mysid shrimp 96-hour LC50 toxicity test results exceeded the limit required by the EPA rendering the system usable in the Gulf of Mexico. Based on lab generated data and results of seabed surveys, the system can be environmentally accepted for potential use offshore UK, Norway and West Africa and other environmentally sensitive areas.

Discussion

Fluid formulated with IO base oil shows stable properties

after heat aging for 24 and 72 hours at 300° F. The HPHT and the emulsion remained stable indicating the absence of hydrolysis. Drill solids contamination resulted in a relatively small change in the properties especially in high temperature testing.

Conclusion

An improved, more biodegradable synthetic drilling fluid can provide performance equal to conventional invert fluids at different oil water ratios, at high density, under high temperature conditions and in the presence of common contaminants encountered while drilling.

Based on research data the rate of biodegradation of a synthetic fluid can be enhanced several folds with the addition of booster fluid thus making it more compliant for use in environmentally sensitive areas.

Toxicity and bioaccumulation tests conducted on this system indicate that cuttings impregnated with this fluid can be discharged offshore, causing minimal harm to marine life organisms.

Preliminary results from the sea bed surveys conducted in a deep water offshore environment confirmed that this biodegradation enhancement approach is of a high ecological importance. It allows the oil on the seafloor to biodegrade faster, thus a faster recovery of the sea bed environmental equilibrium.

The use of this greener fluid can minimize and possibly eliminate the usually high cost associated with hauling, treatment and disposal or injection of drill cuttings.

Acknowledgement

The authors wish to thank TotalFinaElf and Baker Hughes Inteq for permission to publish this paper. The work, test protocol and organization, and fruitful discussions and comments provided by staff from both companies were very much appreciated. Special thanks go to Frederic Aubry for the lab work and effort and to Steve Watson for his comments and support.

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SI Metric Conversion Factors

bbl × 1.589873	E-01 = m ³
gal × 3.785412	E-03 = m ³
cp. × 1.0	E-03 = Pas
inch × 2.54	E+00 = cm
lbm × 4.535924	E-01 = kg
ft × 3.048	E-01 = m
psi × 6.894757	E+00 = kPa
psi × 6.894759	E-02 = bar
ppg × 2.853	E+00 = kg/m ³
lbm/gal × 1.198264	E+02 = kg/m ³
lb/100 ft ² × 4.788026	E-01 = Pa
(°F-32) ÷ 1.8	E+00 = °C

Table 3 - Evaluation of booster components

Composition	Phosphorus 3	Phosphorus 1	Phosphorus 2
Density, ppg	11.0	11.0	11.0
O/W ratio	80/20	80/20	80/20
Base fluid, ml	0.561	0.561	0.561
Fatty acid, ml	34.1	34.1	34.1
Organic N2, gm	27.4	27.4	27.4
Phosphorus 3, ml	41	-	-
Phosphorus 1, ml	-	41	-
Phosphorus 2, ml	-	-	41
Initial Properties			
600/300	93/56	121/84	160/106
200/100	42/27	68/51	86/68
6/3	7/6	24/22	60/27
PV	37	37	54
YP	19	47	52
10sec/10Min Gels	7/8	21/27	28/45
E.S, Volts	780	1380	1220
Hot Roll Properties			
	@300°F	@300°F	@300°F
600/300	69/43	66/39	157/91
200/100	33/21	30/19	75/47
6/3	9/8	6/5	7/4
PV	26	27	66
YP	17	12	25
10sec/10Min Gels	8/12	6/8	5/10
E.S, Volts	530	290	270
HTHP (300°F), mls	6	4	3

Table 4 - Biodegradation – oxygen consumption (mg/l) versus days – Base oils

Days	Control Olive Oil	Oil A Olefin	Oil B Paraffin	Oil C Exp Olefin	Oil D Ester
0	0	0	0	0	0
1	813	1341	288	201	3394
2	867	1551	383	271	4063
6	1145	2108	504	355	6532
8	1710	2433	537	380	7394
12	1942	3146	630	443	9880
14	2114	3487	685	493	14416
16	2420	4058	785	533	16961
20	2655	5125	1051	561	21206
22	3016	5705	1141	573	21685
26	3429	8830	1521	649	21751
32	3603	10410	1935	662	21800
34	3670	11058	2082	676	21812
36	3694	11709	2209	689	21831

Table 6 - Effect of booster on fluid stability

Fluid number	1	2	3	4	5	6	7	8	9	10	11
ISOTEQ, liter	613.05	584.60	516.58	417.95	516.58	516.58	516.58	516.58	516.58	516.58	516.58
Fatty Acid, l/m3	40.83	39.00	34.14	27.62	34.14	34.14	34.14	34.14	34.14	34.14	34.14
Phosphorus 3, l/m3	48.60	46.00	40.95	33.13	40.95	40.95	40.95	40.95	40.95	40.95	40.95
Organo-Clay, kg/m3	17.00	17.00	17.00	17.00	17.00	17.00	17.00	17.00	17.00	17.00	17.00
Emulsifier, kg/m3	15.70	15.70	15.70	15.70	15.70	15.70	15.70	15.70	15.70	15.70	15.70
Wetting agent. Kg/m3	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30
Lime, kg/m3	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00
Water, l/m3	176.77	155.00	151.54	125.45	151.54	151.54	151.54	151.54	151.54	151.54	151.54
CaCl2, kg/m3	58.13	46.50	49.83	41.25	49.83	49.83	49.83	49.83	49.83	49.83	49.83
Organic N2, kg/m3	32.29	31.00	27.24	22.04	27.24	27.24	27.24	27.24	27.24	27.24	27.24
F.L. reducer, kg/m3	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Barite, kg/m3	--	203.0	604.2	1222.3	604.2	604.2	604.2	604.2	604.2	604.2	604.2
Drill solids, %	--	--	--	--	3.00	6.00	9.00	3.00	3.00	300	300
Salt water, %	--	--	--	--	--	--	--	5.00	15.00	--	--
Aging Temp, °F	180	180	180	180	300	300	300	300	300	300	300
Aging Time, Hours	16	16	16	16	16	16	16	16	16	48	72
Oil Water Ratio	80/20	82/18	82/18	80/20	80/20	80/20	80/20	75/25	69/31	80/20	80/20
PROPERTIES @ 120 °F, after Hotrolling											
Density, sg	0.97	1.10	1.44	1.84	1.45	1.48	1.51	1.43	1.41	1.44	1.44
Fann 600 rpm	28	34	69	119	85	90	105	86	110	60	47
Fann 300 rpm	17	21	43	72	50	50	59	49	68	34	25
Fann 6 rpm	3	4	9	13	6	3	6	4	10	4	2
Fann 3 rpm	2	3	8	12	5	2	5	3	8	3	2
PV, cps	11	13	26	47	35	40	46	37	42	26	22
YP, lb/100ft2	6	8	17	25	15	10	13	12	26	8	3
Gels, lb/100ft2	3/5	4/6	8/12	13/18	6/8	3/6	6/10	5/8	10/11	4/5	2/5
HPHT 300°F/500 psi	11	7	6	5	34	30	28	34	28	56	80
E.S, Volts	260	330	530	480	220	260	240	170	130	320	120

Table 7 - Toxicity data – booster with Phosphorus 3

Test Method	Result
Sediment Reworker Test using Leptocheirus plumulosus	96 hr. LC50 = >27 ml/kg
Drilling Fluids Toxicity Test using Mysidopsis bahia	96 hr. RF =54,7000 ppm SPP

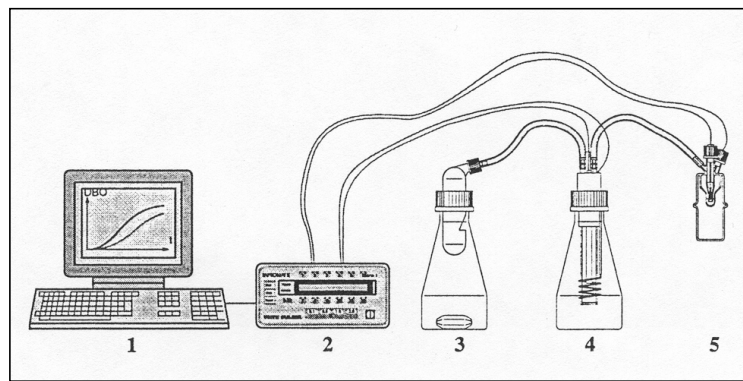
Table 8 - Fluid effects on volume and hardness of various elastomers

Test Temp./Pressure, °C/psi	179/5000	179/5000
FKN, Fluoroelastomer, Viton	30.70	Brittle
FEPM, Aflas	13.80	-5
NBR, Nitrile	3.85	0
HNBR, Hydrogenated nitrile	9.76	-5
NITRILE	--	--

Table 9 - Fluid effects on specific physical characteristics for selected elastomers

Elastomer	TestDuration	Temp., °C	Volume Change, %	Hardness Change, %	T. Strength chg., N/mm ²	Elongation Change, %	Reactivity 1=low,3=high
F	72 hr	150	-0.6	-3	-2.5	-25	1

Test Protocols: ASTM 0471, DIN 53521, DIN 53519, and DIN 53504

Figure 1 - Schematic of the Sapromat

1/2: Recorder/Control Panel
3: Reactor

4: Oxygen supplier
5: Pressure Gauge

Figure 2 - Evolution of the rate of biodegradation of IO base

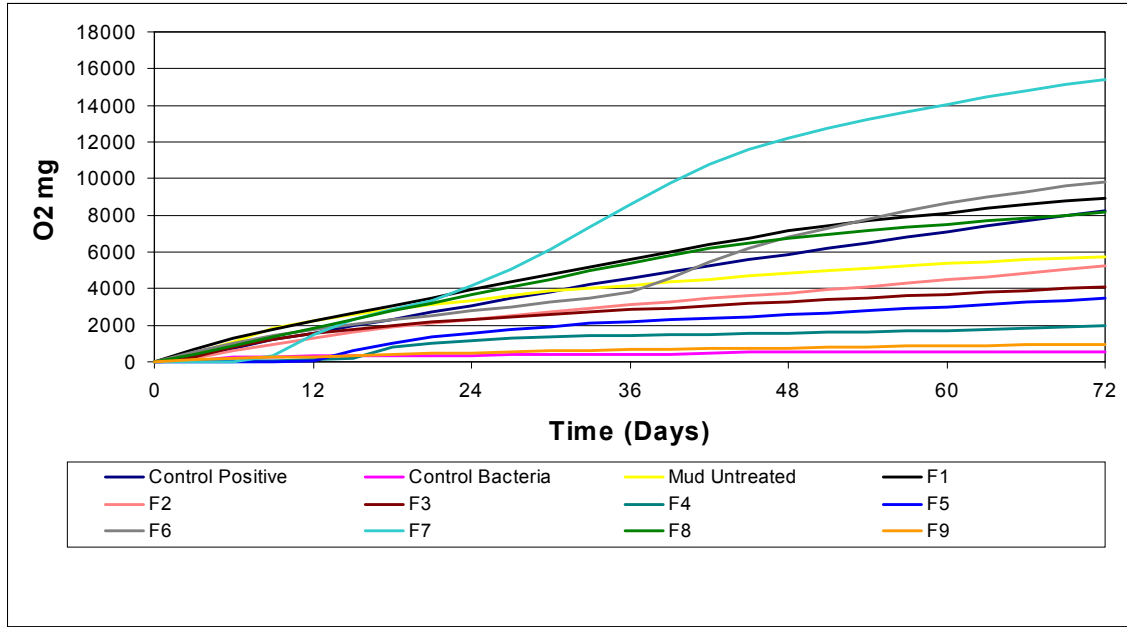


Figure 3 - Evolution of the rate of base oils biodegradation

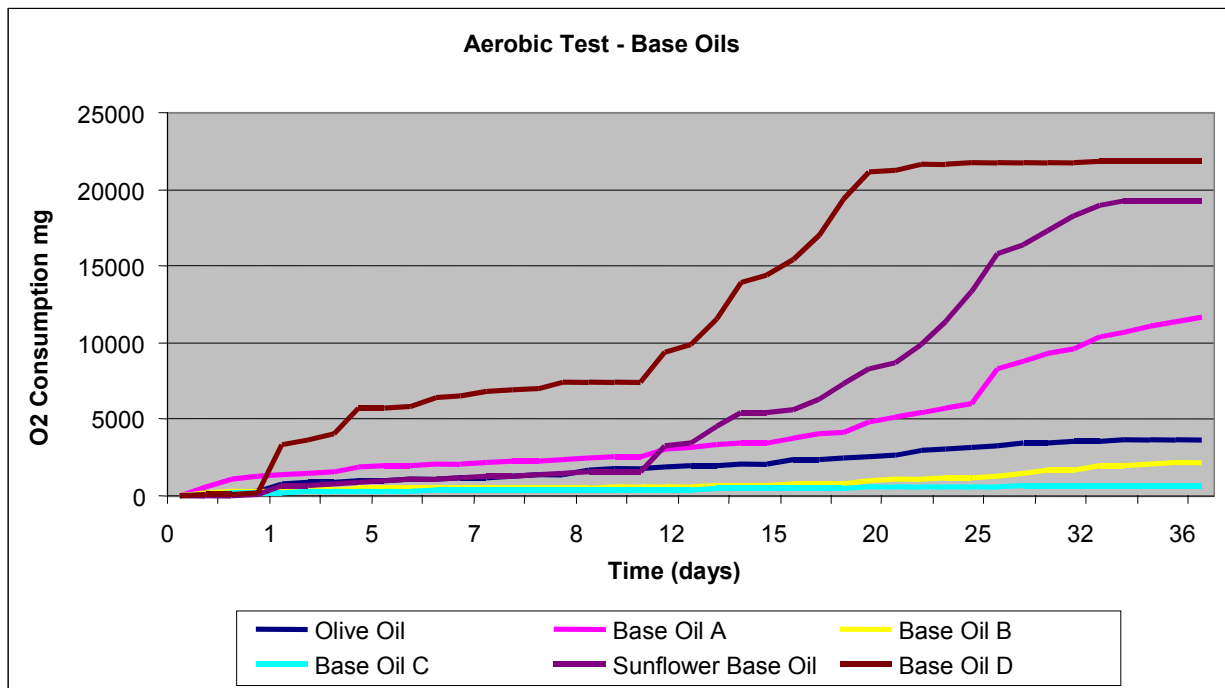


Figure 4 - Evolution of the rate of biodegradation - muds with Phosphorus 3

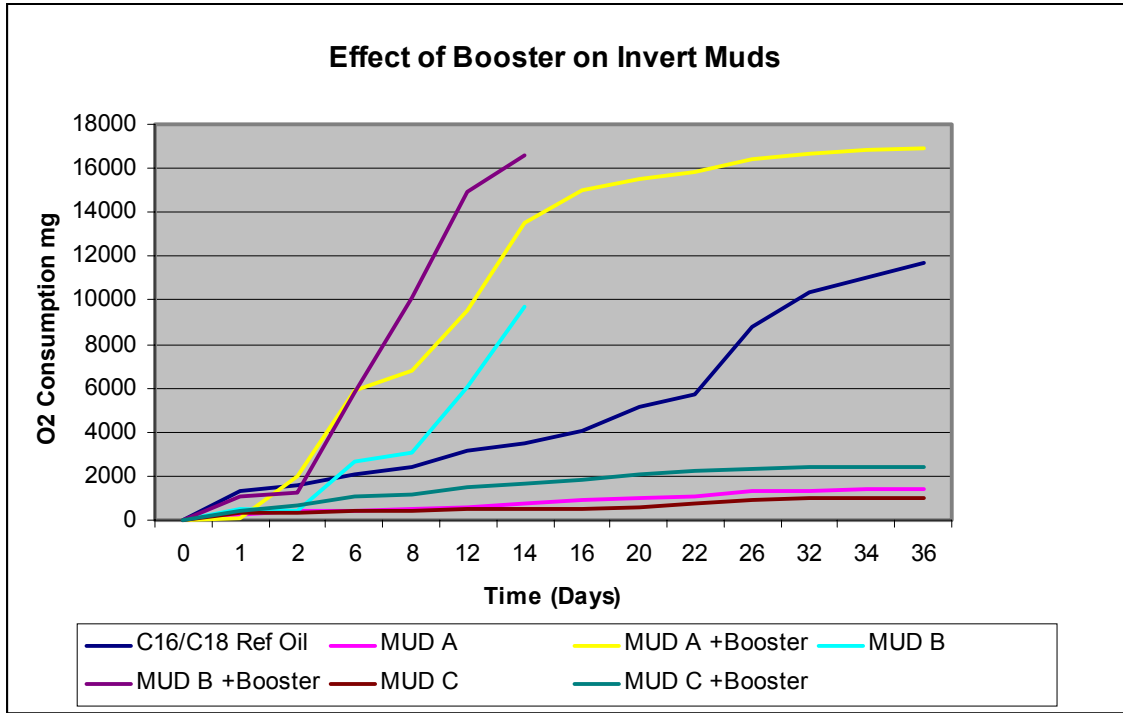


Figure 5 - Yield Point Evaluation of booster fluids on weighted fluids

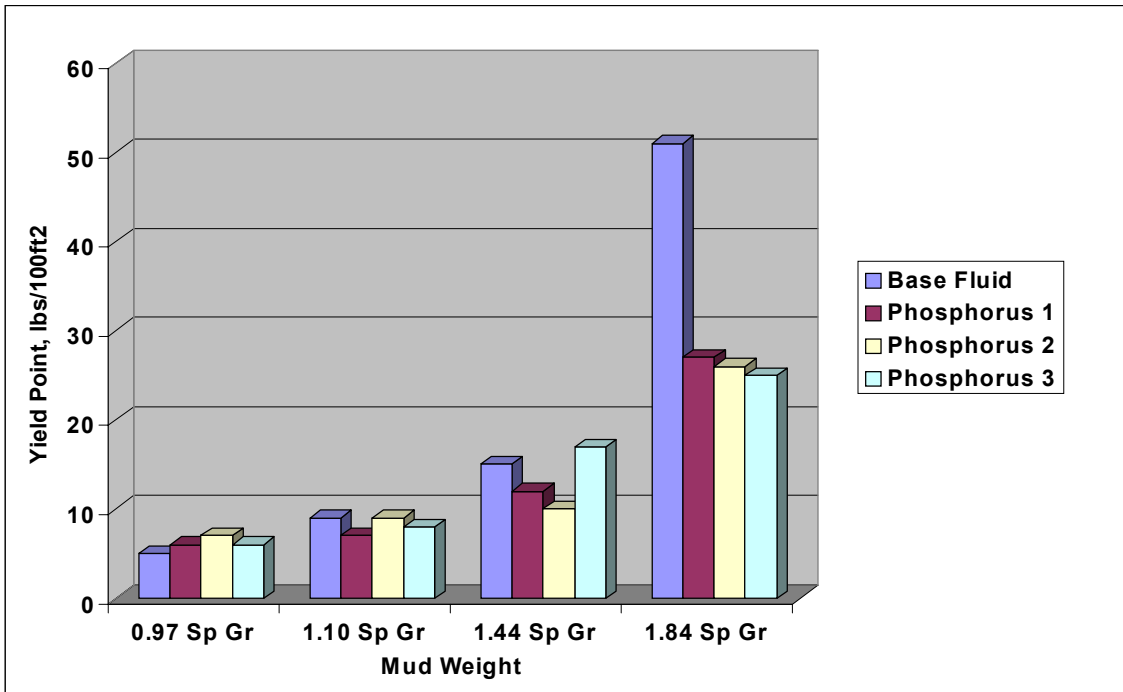


Figure 6 - Electrical Stability Evaluation of booster fluids on weighted fluids

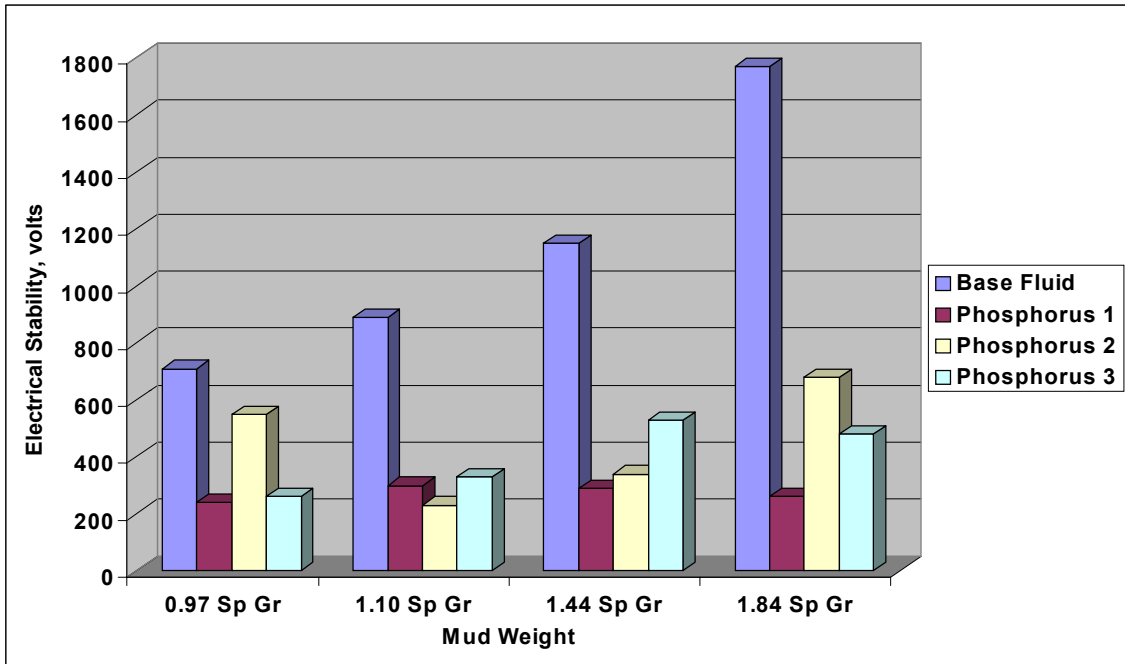
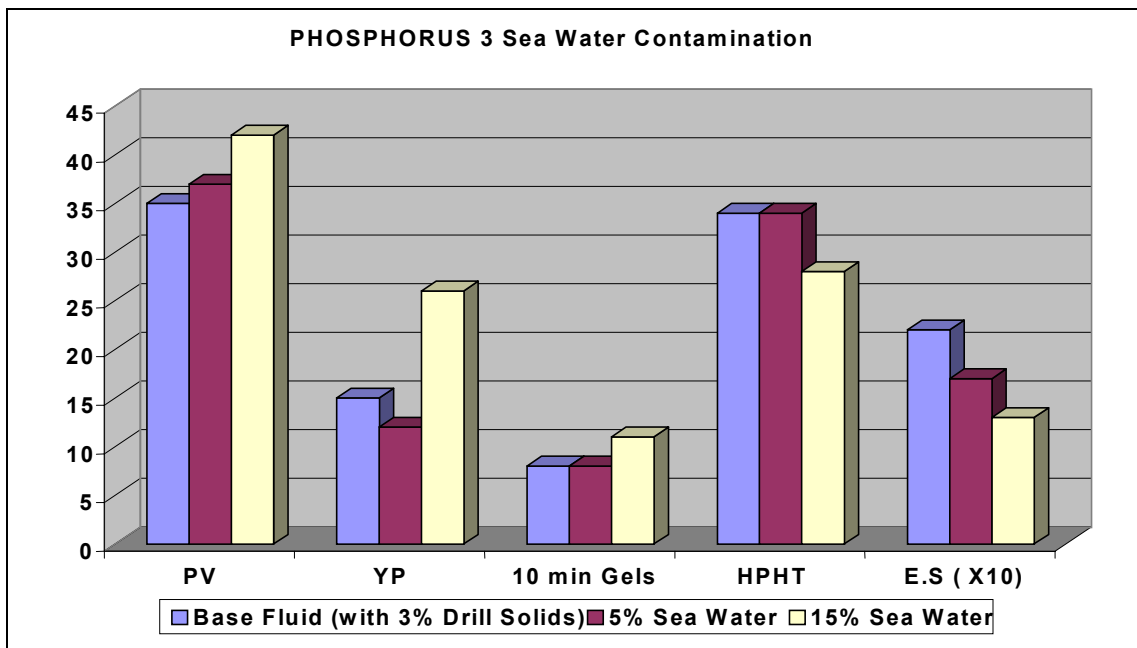
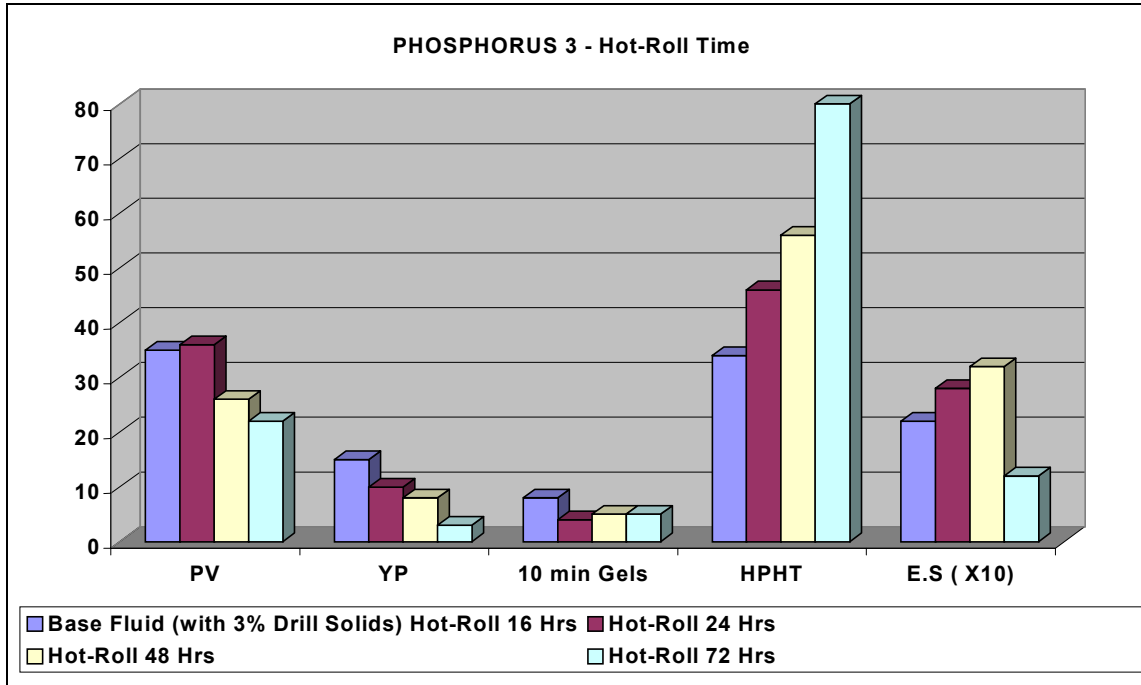


Figure 7 - Evaluation of seawater contamination on mud properties



Figures 8 - . Evaluation of time stability on mud properties



Glossary

PV = Plastic Viscosity

YP = Yield Point

HTHP = High temperature High Pressure

E.S = Electrical Stability

OWR = Oil Water Ratio

M.W, SG = Mud weight, Specific F.L Reducer = Fluid Loss Reducer