



## Progression of Water-Based Fluids Based on Amine Chemistry – Can the Road Lead to True Oil Mud Replacements?

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### Abstract

Ammonia-derived chemicals including amines, amides, polyamides, imines, nitriles and amino acids are used in many water-based drilling fluid components. Addressed in this paper are those derivatives, which contribute to clay and shale stability.

Ammonium chloride was tested more than 30 years ago as a shale inhibitor. Diammonium phosphate has been used for more than 20 years. Organo-amines were more recently introduced. Relatively simple organic amines were first added to drilling fluids 15 years ago to enhance cuttings and wellbore stability. Offering performance approaching that of potassium cation, simple amines effectively carry on in many regions for specific applications. Complex amine chemistry is now better understood and the application of such compounds in the field is increasing. Several classes of diamines and polyamines provide a basis for effective water-based fluids that have been used to replace synthetic-based drilling fluids on several offshore wells.

An extension of the latest amine technology has enabled design of a membrane-forming water-based fluid with near 100% membrane efficiency. Recently introduced amine-based fluid designs are engineer friendly, reduce dispersion and hydration of clays, reduce drilling costs, and promise to provide shale stability at surprisingly high temperatures

### Introduction

Shale instability is a continuing and costly drilling problem despite increasing use of **non-aqueous fluids (NAF)** which include mineral oils, esters, olefins, or other non-aqueous carriers. Shales make up more than 75% of formation drilled and cause in excess of 90% of wellbore-instability problems. Use of non-aqueous and highly inhibitive water-based drilling fluids (WBM) have not eliminated shale-related wellbore instability problems. The majority of drilling problems are attributed to water sensitivity of shale.<sup>1</sup>

The characteristic benefits of invert emulsion drilling fluids are usually cited as the technical goals of an "ultimate" water-based mud. Improved shale stability is attributed to use of NAF because of their non-aqueous character. Properly formulated NAF contain emulsifiers and surfactants which embed water or brine in an internal phase and cause "oil" wetting of the contacted

rock. The isolated aqueous phase and induced wettability changes prevent or delay hydration of clays within sensitive shales. The non-aqueous carrier fluids of NAF readily wet the surface of drilled shale but do not freely enter the permeable porous matrices of the rock itself. The non-aqueous carrier cannot enter pores of the rock because the water-wetted character of the shale pores is maintained by a capillary effect.<sup>2</sup> A significant differential pressure of hundreds to thousands of pounds per square inch is required to displace water wetting the inside of shale pores. The pressure required depends upon the pore size and the wettability characteristics of the NAF.<sup>3</sup>

The emulsified internal phase of NAF, is a discontinuous aqueous dispersion, usually a brine, typically a solution of calcium chloride of 100,000 to 300,000 mg/L. The emulsified aqueous brine phase is isolated from the shale pores by a non-aqueous film of emulsifier-surfactant and carrier fluid. This film serves as a semi-permeable membrane and allows an osmotic pressure differential to develop across the surface of the shale rock. The osmotic pressure is measurable and controllable by adjustment of salt concentration and surfactant chemistry and concentration.

Consequently, these NAF have two easily established characteristics which prevent contact of shale with water and contribute significantly to shale stabilizing characteristics of the fluids. These NAF characteristics serve as design targets to many researchers of aqueous-based system seeking to achieve NAF system performance when using a WBM.

The shale-stabilizing advantages of NAF have associated costs. Additional costs of NAF include, but are not limited to, the actual purchase price of the fluid, environmental considerations, disposal concerns, health and safety issues, and detrimental effects on the drilling operation or reservoir performance. The increased risk of circulating losses when drilling with a NAF can negatively affect the economics of a drilling operation. The same capillary effect described above, while preventing ready penetration of the formation by drilling mud base fluid, may contribute to serious whole NAF losses to induced fractures. The full hydrostatic pressure of the fluid column is available at the drilling fluid-shale interface. Increased stresses can cause increased fracture roughness, increase in fracture

conductivity, and loss of fracture compliance.<sup>4</sup> Rock fracture results in loss of tens of thousands of barrels of invert emulsion and synthetic drilling fluids every year.

Induced rock fracturing is not as evident when drilling with water-based drilling fluids presumably because the hydrostatic pressure differential extends deeper into the surface of the formation. Distribution of wellbore stresses more deeply into the formation helps avoid stress concentrations, fracturing, or fracture roughness.

Observations in the field suggest that developed fractures heal more readily when induced with water-based drilling fluids. Fractures induced with WBM are more readily sealed with conventional "lost circulation material". Fracture healing may be facilitated by otherwise detrimental hydrational effects and clay swelling.

It is easy to imagine, that by analogous mechanism, aqueous-based fluids might provide similar benefits. When exposed to conventional water-based drilling fluids, shales will have an immediate tendency to take up water from the drilling fluid. Depending on the chemical characteristics of the shale, this can result in a rapid swelling or dispersion of the shale matrix due to an increase in pore pressure within the shale. Altering the chemistry of the aqueous phase (e.g. by inclusion of high concentrations of anions) can slow down the water uptake, or by including some active cations (e.g. potassium or calcium) the potential for shale matrix separation can be reduced. In addition high-molecular-weight "plugging" materials (e.g. PHPA, cloud-point glycols) can be added to physically try to block the capillary network on the shale surface. All of these mechanisms can be used to slow down the process of water uptake, however in an aqueous environment, the overall mechanism of water uptake into the shale matrix will prevail and the shales will fail over time.

For 50 or more years, hundreds of chemical concoctions have been prepared from water and brines which through a variety of mechanisms might be claimed to somehow retard swelling of clays within shales. Some of the earliest of these aqueous fluids were based on sodium chloride and starch; silicate muds have been tested; lime muds and dispersed calcium sulfate-based fluids were of interest for many years.

Enthusiasm for KCl/polymer drilling fluids began at the close of the 1960s.<sup>5</sup> KCl is defined as the starting point for this revisit of the evolution of ammonium and amine-based drilling fluids.

In the early 1970s potassium, usually as a chloride salt, was added to drilling fluids and found to be an effective inhibitor for clay swelling. With ongoing application of the then almost exotic salt, some understanding of "clay chemistry" and the correct chemical jargon became essential for the ambitious mud engineer. An "osmotic effect" was attributed to the potassium chloride/PHPA muds which may be more correctly called suppression of osmotic swelling.<sup>6</sup>

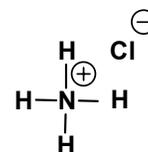
Osmosis, membranes, and hydrated ion diameter were serious topics of conversation, sometimes even at the wellsite.

Another cation which promised to be as effective as potassium was the ammonium ion  $< \text{NH}_4^+ >$ . This understanding, it can be argued, led to development of simple mud additives, complex long-chain polymers, surfactants, and substituted glycols, to mention a few, which contained ammonium, quaternary amines, amides among other nitrogen-centered derivatives. This paper will briefly revisit 11 nitrogen-centered additives, discuss a new amine technology, and present the next steps in the evolution of amine chemistry in drilling fluids.

## History of Ammonium and Amine-Based & Treated Mud Systems

### Ammonium Salt Mud Systems

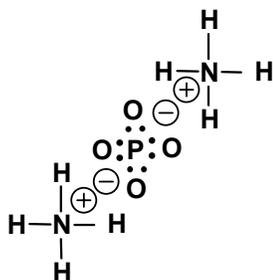
Ammonium chloride salt substitutes an ammonium ion for potassium as an effective inhibitive cation. Both ammonium and potassium have been reported with similar hydrated ion diameters<sup>7</sup> at typical drilling fluid pH. Intuitively, many would presume that the two salts should perform equally well. However, operationally, ammonium chloride,  $\text{NH}_4\text{Cl}$ , was found to be a real troublemaker with its free liberation of ammonia gas as mud pH climbed. Apparently in the 1960s it was, and remains, impossible to prevent mud engineers or derrickmen from adding an extra sack of caustic soda to the mud system. Waves of ammonia gas cleared the drill floor, probably on the first and last well that ammonium chloride salt was evaluated. The same pH sensitivity problem can manifest itself when drilling green cement.



Another ammonia-based inhibitive salt added routinely to field muds was fertilizer-grade diammonium phosphate or DAP. DAP buffers the drilling fluid to a pH of about 8 and use of additional caustic soda is not so tempting. Combination of DAP and polyanionic cellulose, PAC, was recommended as a system in the early 1970s as a cheap and environmentally friendly replacement for saturated salt muds. DAP-PAC muds received attention again in the late 80s in the Rockies because of their lack of chlorides and improved environmental acceptability.<sup>8</sup> Temperature and performance limitations confined the material to a narrow market.

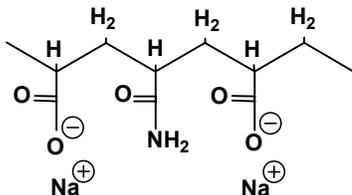
Maximum temperature practicable for such phosphate-treated drilling fluids is about 150°F.<sup>9</sup> DAP-

based muds have long had a market in California because of their ability to tolerate a high content of 60-70 lb/bbl low-gravity solids typical of the low temperature and shallow wells drilled using rigs with minimum or no solids-control equipment. The pH buffering of DAP muds makes them somewhat more resistant to increases in pH. Drilling green cement can cause breakout of ammonia gas and release at the bell nipple and flowline.



#### PHPA - Partially Hydrolyzed Polyacrylamide

“Partially hydrolyzed polyacrylamide” or PHPA can be viewed as an anionic cousin of ammonium cation-based systems. The first field test of a PHPA potassium chloride drilling fluid was run in 1969 in the foothills area of Canada.<sup>5</sup> PHPA and variants continue to be used in many inhibitive mud formulations. In PHPA muds used in the North Sea, potassium chloride is preferred as the exchangeable cation to replace or exclude sodium and prevent clay swelling. For US “deep water” drilling in the Gulf of Mexico PHPA is used with an industry standard 18-22% sodium chloride.<sup>10</sup>



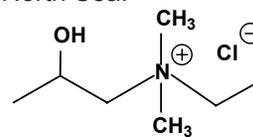
Occasionally DAP has also been used to provide the inhibitive cation in PHPA treated drilling fluids and is effective in low temperature applications.

The degree of “hydrolysis” of PHPA is significant. The standard 30% hydrolyzed PHPA variety preserves shale stability via attraction of the anionic sites along the polymer chain to the cationic sites on the edges of the clay platelets. It is likely that the hydrolyzed anionic sites on the 30% hydrolyzed polymer more closely match the spacing of substitutable sites on clay platelets.<sup>11</sup>

#### Organic Cationic Materials – Quaternary Cationic Polymers

In 1989 polyamines with cationically charged groups were introduced.<sup>12</sup> Cationic polymers come in several flavors, but early Amoco work applied quaternized

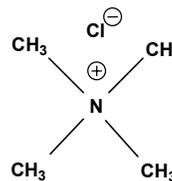
poly(dimethylamine-co-epichlorohydrin on a series of wells drilled in the North Sea.<sup>13</sup>



The cationic quaternized amine group is strongly adsorbed on the clay, reducing its charge and repulsive forces, inhibiting swelling and dispersion. Typically these polymers may contain anywhere from 400 to 7500 cationic sites. This means that association of the polymer with clay is essentially an irreversible process.<sup>14</sup> Cationic polymer systems may be the most inhibitive of water-based fluids. The cationic polymers appear to adsorb on the negatively charged clay-mineral surfaces. The adsorption mechanism is consistent with an ion-exchange reaction. Exchangeable cations in the surface clay lattices are replaced by a pendant cationic group from the polymer. This was shown in a simple lab experiment where a suspension of API bentonite in de-ionised water was mixed with a solution of cationic polymer in de-ionised water. Measurements on the filtered water 2 hours after mixing demonstrated a reduction in the cationic polymer concentration and a marked increase in both soluble sodium and calcium content indicating cation exchange had taken place. The polymer is very large compared to simpler cationic materials. The size of the molecule prevents penetration into pores of shale or low-permeability producing zones. The permanency of its association with clays is likely to cause formation damage in higher permeability, shaley producing zones. Cationic polymers are typically applied in a range of 3 to 8 lb/bbl concentration. Due to high consumption (leading to high related cost and engineering difficulties) and high marine toxicity, the cationic polymers originally developed are not widely used today.

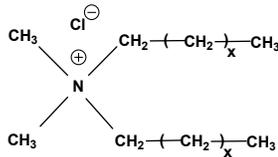
#### Organic Cationic Materials – Quaternary Alkylamines

Patented in 1988 was an application for tetra methyl ammonium chloride or TMAC. TMAC, marketed as a “potassium substitute”, is an elegantly simple and intriguing but toxic molecule. The application patent holder and distributors of TMAC claim that only 1/10 the concentration compared to potassium chloride is required to provide clay inhibition and shale stabilization.<sup>15</sup>



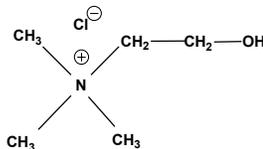
The low treatment concentration reduces chloride anion introduced to frac fluids or muds and enables a degree of shale stability on land jobs with anion or conductivity restrictions. With a molecular weight of only 74, the tetra methyl ammonium cation is small and mobile. An MSDS lists an LD<sub>50</sub> (rat) for TMAC of 50 mg/Kg. Toxicity is mitigated somewhat as TMAC readily combines with clays which allow it to pass most oilfield toxicity studies. TMAC is readily absorbed through skin and personal protection is necessary. TMAC does not have widespread application in drilling fluids but is applied in frac fluids.

Several variations on TMAC have been described including tetra-alkyl ammonium chloride and dimer and trimer versions of the molecule. Used with the cationic polymers discussed above, Amoco selected two of what the company called "quaternary ammonium surfactants" in 1989. The quaternary alkyl amines used were dimethyl dialkyl ammonium chloride and trimethyl alkyl ammonium chloride. The dialkyl version presented here was configured with x equal to 10 or 16.



### Organic Cationic Materials – Quaternary Hydroxy Amines

High-molecular-weight cationic polymers have a large molecular size and cannot penetrate the clay layers as effectively as a low-molecular-weight monomers or oligomers. As a result, adsorption of high-molecular-weight polymers occurs primarily on the exterior surfaces of shale or cuttings as an encapsulating coating. Consequently, desorption of exchangeable cations and reduction of cationic exchange capacity are less significant when compared to low-molecular-weight materials.<sup>16</sup> Low-molecular-weight cationic materials may be regarded as "hydration suppressants" rather than cationic encapsulators. A very effective and non-toxic low-molecular-weight quaternary monoamine material is the patented<sup>18</sup> chemical, β-hydroxyethyl-trimethylammonium chloride (HETMAC).

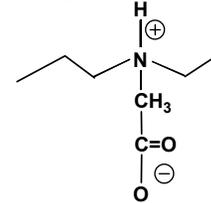


With a molecular weight of 104, the cation can easily penetrate shale pores and serve as a potassium substitute at relatively low concentration. HETMAC is a non-toxic chemical that has primarily been used

medically. Laboratory tests have shown that 5 to 6 lb/bbl of HETMAC provides inhibition equivalent to 6% KCl. Unlike KCl, HETMAC maintains its effectiveness in muds containing moderate amounts of sodium chloride. This effective, efficient amine continues to be widely used.

### Amphoteric Poly-amino Acids

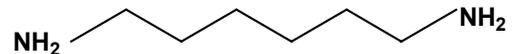
In 1993 an innovation introduced both cationic and anionic character to a single molecule.<sup>18</sup>



Amine and a carboxylic acid groups were combined in a polymeric configuration. The correctly sized amphoteric hydration suppressant when used at a pH between 5 and 9 can satisfy all charges on a clay particle. The amphoteric chemical, a synthetic complex amino acid,<sup>19</sup> displays shifting anionic-cationic behaviour with pH change over the applicable range. The chemical is compatible with both anionic and cationic mud additives. This amphoteric material has been widely used in Canada, South America, and in Eastern Europe. The small molecular size and amphoteric character make these poly-amino acids especially useful as clay hydration suppressants in "drilling-in fluids". Clays in shales and in permeable sands can be stabilized and a damaging decrease in permeability prevented.

### Alkyl-diamines

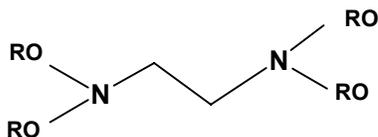
A less toxic, yet effective, replacement for TMAC was introduced by D. Horton and A. Jones in 1996.<sup>14</sup> Hexamethylene diamine (HMDA) is primarily marketed by frac and stimulation companies. Based on CST test, performance, 0.75% HMDA is equivalent to 0.15% TMAC. The application patent covers several members of the alky amine family.



### Polyamine-glycols

There were two very effective amine glycols introduced in the mid-1990s.<sup>20</sup> Unlike other available glycols these proprietary products did not require potassium chloride for optimum performance. The interesting non-cloudpoint glycols provided a degree of shale stability in fresh water and were very effective in sodium chloride brines. The glycols were able to effectively bind within the shale layers by cationic substitution and fix clay spacing. Apparently "the amine group bound the molecule to the clay minerals and the glycol groups stabilized the clay".<sup>20</sup> Addition of these types of materials to previously used

muds with more than 15 lb/bbl of previously dispersed low-gravity solids could cause unmanageable flocculation.

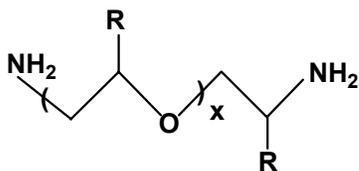


These glycols and newer variants demand to be treated as fundamental components of a freshly prepared base mud and not as simple additives. A member of this unique chemical family provided the best shale stabilizing characteristics of all the glycol-treated muds tested in a one joint industry study performed in 2000-2001. In 1996 on a well in the Gulf of Mexico, without an effective anti-accretion additive yet available, the efficiency of the material led to sometimes frustrating bit and collar balling. Due to cost considerations and misunderstanding of proper application these variant glycols never achieved widespread use in the US.

### New Amine Technology and the HPWBM

#### Ether/Glycol Polyamines

A key inhibitive ingredient of a new high performance water-based mud (HPWBM) is a material similar to the polyamine glycol. A novel ether amine was introduced last year to the Gulf of Mexico. This ether amine<sup>21</sup> is one component of a mud system which includes a relatively short-chain, mildly cationic terpolymer, an effective anti-crete additive and efficient filtration control additives of narrow molecular-weight distributions. A typical formulation is presented in Table 1. Drilling fluids formulated around these primary components have shown a high degree of flexibility; good inhibition performance has been seen using base fluids as varied as freshwater to saturated NaCl. Unlike the earlier cationic polymers the ether amines do not show a tendency for high polymer depletion on exposure to active shale, and are considered to be of low toxicity.



#### HPWBM Performance Tests

Several formulations are shown in Table 1 which describes variants of a new amine-based HPWBM. The variants include conventional and membrane-forming versions. Also included is a comparative formulation for a PHPA system. In all cases the new HPWBM greatly

surpassed PHPA drilling fluid performance and more closely resembled the reference invert emulsion drilling fluid.

#### Shale Stability – "Slaked Durability" Test

In the Slaked Durability test cuttings were rolled and physically stressed in a rotating "squirrel cage" type screening device. Cuttings remaining at the end of the test were weighed and the percentage recovery reported. The test demonstrates a 31% increase in shale stability at pH 9 when a proprietary polymer additive is added to HPWBM formulation. At pH 10 recovery values were equal or slightly better than recovery from standard HPWBM but differences were not dramatic. Data is presented graphically in Fig. 1. Test details are presented in Table 2.

#### Shale Stability – Conventional Hot Roll Evaluation

Conventional hot roll stability test data for the HPWBM series is presented graphically in Fig. 1. HPWBM at pH 9 with or without the polymeric additive displayed excellent recovery values. Cuttings appeared to be slightly more intact than cuttings rolled in HPWBM with the polymeric additive at pH 10 (HPWBM-4). The recovery trends in this test were not unlike those recorded in the Slaked Durability study. In both cases fluid formulation HPWBM-5 outperformed fluid formulation HPWBM-4. Test details are presented in Table 2.

#### Shale Stability - Bulk Hardness Test

Measurement of shale stability based on retained or supplemented shale hardness is presented in Fig. 2, which compares cuttings hardness measured using a proprietary "Bulk Hardness Tester" that most closely resembles a compact pasta press. After cuttings or broken shale has been hot rolled for a specific period in the drilling fluid of interest, the cuttings are extruded through a perforated steel plate. The force required for extrusion is recorded as "Bulk Hardness". Data includes turns of a feed screw and recorded torque at each unit of rotation. Test parameters are presented in Table 2.

In the presented data, cuttings are tested to compare the stabilizing performance of four variants of an HPWBM drilling fluid. Cuttings rolled in HPWBM containing the membrane-forming additive retained the highest level of hardness. Data collected using a PHPA mud is presented for comparison. Performance of the HPWBM with or without the membrane-forming additive exceeded performance of the PHPA system. The improved performance was observed at low and high pH.

#### HPWBM and Accretion

Accretion tests were run using the same fluids described in Table 1. Fig. 3 presents graphical comparison of

accretion performance of the HPWBM variants one through four. Included for comparison is accretion data for a PHPA and an invert emulsion mud. Photographs of the steel test bars with accreted material are presented as Fig. 4. Accretion results of the HPWBM with membrane-forming additive were superior to the accretion results measured using standard HPWBM and comparable to accretion typical of an invert emulsion drilling fluid.

#### **HPWBM – Comments on Formation Damage**

As was found with HMDA, tests of the new ether amine-based system on Berea sandstone core have demonstrated minimum damage. However, use of an inhibitor will not reduce formation damage caused by solids invasion. Mud solids management must provide suitable particle-size distribution to prevent introduction of damaging mud solids to productive sands

Most basic components of this HPWBM system are intrinsically non-damaging with the exception of barite and drilled solids. However, one secondary component, a proprietary, mildly cationic terpolymer similar to PHPA, can precipitate under certain circumstances. This proprietary acrylamide derivative is not a conventional PHPA and it is more compatible with acid than PHPA. A photographic comparison of a 2 lb/bbl of PHPA and a cationic terpolymer solution, each in 15% HCl, is presented as Fig. 5. The cloudiness of the jar containing PHPA indicates polymer precipitation. The clear fluid in the second jar indicates acid solubility of the cationic terpolymer.

The compatibility of this product with acid over a range of temperature and salinity conditions has not yet been tested. Calcium ion, for example, can be expected to reduce the solubility of the polymer in acid.

#### **Membrane Development and Osmosis**

A research project begun in 1999 led to design and construction of five standard test cells that have now been used to screen in excess of 300 mud formulations since the inception of the project.<sup>3</sup> Several familiar fluid types were found to be membrane formers, based on osmotic pressure development tests. The traditional fluids tested which readily effect a membrane within or on shale include silicate, high concentration sugar-based systems, and invert emulsion-based fluids.

This new HPWBM provides both an efficient membrane and shale stability. The ether amine inhibitor reacts with other additives to form a networked polymer membrane which supports osmotic pressure development in excess of 1500 psi on preserved West African and outcrop Pierre 1E shales. The detached polymer membrane which formed on a 1-inch diameter shale core is clearly visible in Figure 6.

Work with polyacrylates, sugars, and glucosides led to an understanding of the role played by low-molecular-weight polymers in membrane development in and on

shale. Low-molecular-weight polymers from several suppliers were tested and while a variety of cellulose derived and polyacrylate oligomers provided enhanced osmotic pressure, one proprietary material remained consistently interesting throughout testing during 2001 and 2002.

The acid-soluble oligomer compared favorably to similarly performing proprietary acrylic acid derived oligomers. The experimental oligomer is totally soluble in virtually all types of aqueous-based fluids including KCl-polymer, calcium-based muds, bromide and formate-based fluids, and the currently used ether amine inhibited HPWBM systems used in the Gulf of Mexico, Canada and southern Europe.

This very soluble oligomer provides both the sub-unit for a highly crosslinked polymer membrane and contributes to shale stability and improved HTHP filtrate control. The two personalities of the new HPWBM can be seen with change in pH. At pH above 9.5, a crosslinked-polymer membrane readily forms to coat the formation. At lower pH, the material does not readily polymerise but supports clay inhibition and stabilization. Available amine and oligomeric additive can easily enter the lamellae of the clay and serve as a complementary hydration suppressants.

The original fluid evaluation was performed using donated preserved West African shale. The majority of shale/clay membrane development work was run in 20% salt-based muds. Gulf of Mexico deepwater wells typically specify 20% sodium chloride for suppression of gas hydrate crystallization in the drilling fluid.<sup>10</sup> The 20% sodium chloride concentration also serves as an osmotic driver. The calculated potential osmotic pressure development available from a 20% salt solution separated from de-ionized water by a semi-permeable membrane is approximately 3500 psi.<sup>3</sup>

The potential of one such 20% NaCl brine-based mud is seen in Fig. 7. The chart displays the applied mud pressure labeled as "wellbore and confining pressure". The chart displays the developing pore pressure labeled as "reservoir pore pressure. If no osmotic potential exists due to lack of membrane efficiency, reservoir pressure stabilizes to within a few psi or equalizes to wellbore pressure in a relatively short time.

The test presented as Fig. 7 demonstrates substantial osmotic pressure development in excess of 1500 psi. The near horizontal curve implies that membrane efficiency is near 100% up to the developed osmotic pressure differential of 1500 psi; there is limited exchange or movement of water or ions across the membrane.

This membrane-forming technology can be established in many types of water-based muds but it is a natural extension of the amine-based HPWBM system. A proprietary oligomer additive is used with the HPWBM to generate a membrane in a polymerization reaction. It

was determined that membrane formation is dependent upon pH. Fig. 8 presents osmotic pressure development curves at pH of 9 and pH of 10. Development of osmotic pressure is indicative of membrane formation. As displayed in Fig. 8, osmotic pressure development at pH 10 is profound. Membrane development is inhibited when pH is reduced.

### Future Amine Development for Water-Based Muds

Drilling fluids applying cationic and anionic nitrogen centered groups have developed steadily for more than 35 years. The earliest applied ammonium salts did not provide acceptable pH or temperature stability for a majority of drilling fluid applications. High-molecular-weight anionic and cationic polymers served as encapsulators of cuttings but not particularly well as clay inhibitors. It was only in the last decade that low-molecular-weight polyamine chemistry and direct measurement of osmotic pressure in water-based muds have come together to permit development of inhibitive fluids which also provide a predictable and measurable osmotic contribution to overall shale stability.

Development is continuing which addresses issues pertinent to amine-based mud chemistry. Developmental goals for the coming years include:

- Extension of amine and oligomer performance to higher temperatures
- Economically tailor oligomers to optimum and consistent molecular weight and configuration for improved filtration control and membrane development
- Source less expensive amines which meet performance expectations.
- Investigate of a broad range of organic and inorganic osmotic drivers which complement membrane development.

### Conclusions

Application, in water-based muds, of an efficient shale membrane and subsequent osmotic pressure development may seem to be a good idea based upon experience with NAF. However, reviews of drilling and laboratory data suggest that osmotic pressure development in traditional water-based muds may create accretion and bit balling problems.

A recently introduced amine-based shale inhibitor has been found to contribute to creation of membrane on or in shale when used with a proprietary oligomer. The membrane effect is controlled by adjustment of pH. Use of the membrane-forming additive at the pH at which tendency to form membrane is greatest yields acceptable cuttings stability as measured by hardness and stability testing. Use of the membrane-forming additive at a pH less likely to support a requisite reversible reaction and membrane formation also yields improved cuttings stability.

The new glycol and ether amines combined with the proprietary oligomer now provide for very easy to run and predictable shale inhibitive water-based muds which can readily and optionally support creation of an efficient shale membrane and high osmotic pressure.

The standard HPWBM reduces bit balling and accretion tendencies as measured in laboratory tests and in field experience. To date >25 well sections have been drilled with the HPWBM with the overwhelming conclusion that correct application of this new amine-based technology can give a water-based fluid performance similar to that of a non-aqueous fluid.

When the proprietary oligomeric additive is applied in a similar HPWBM formulation, cuttings inhibition and resistance to bit balling and accretion can be further improved. The complete membrane-forming drilling fluid system has been demonstrated to provide excellent shale stability and effective accretion control and it is anticipated that the goal of a true non-aqueous fluid replacement will be met with the field use of the system.

The HPWBM and oligomer enhanced HPWBM can effectively replace NAF in selected applications:

- When temperature < 300°F
- When density requirement is < 16 lb/gal
- If the drilled shales are compatible with the HPWBM chemistry for the period of time required to drill and case and interval.

### Acknowledgments

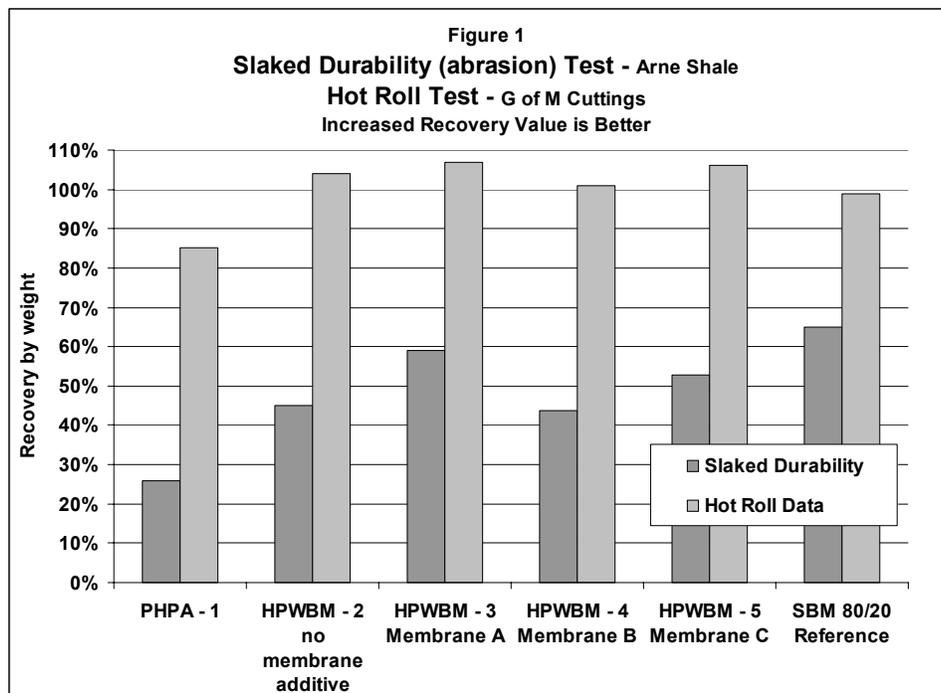
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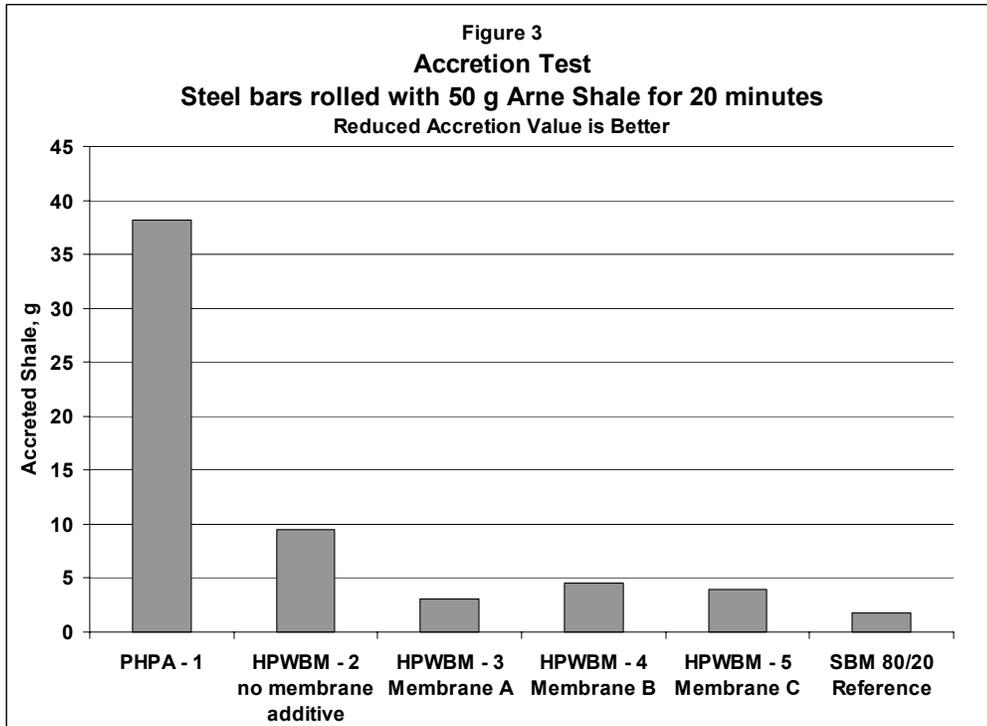
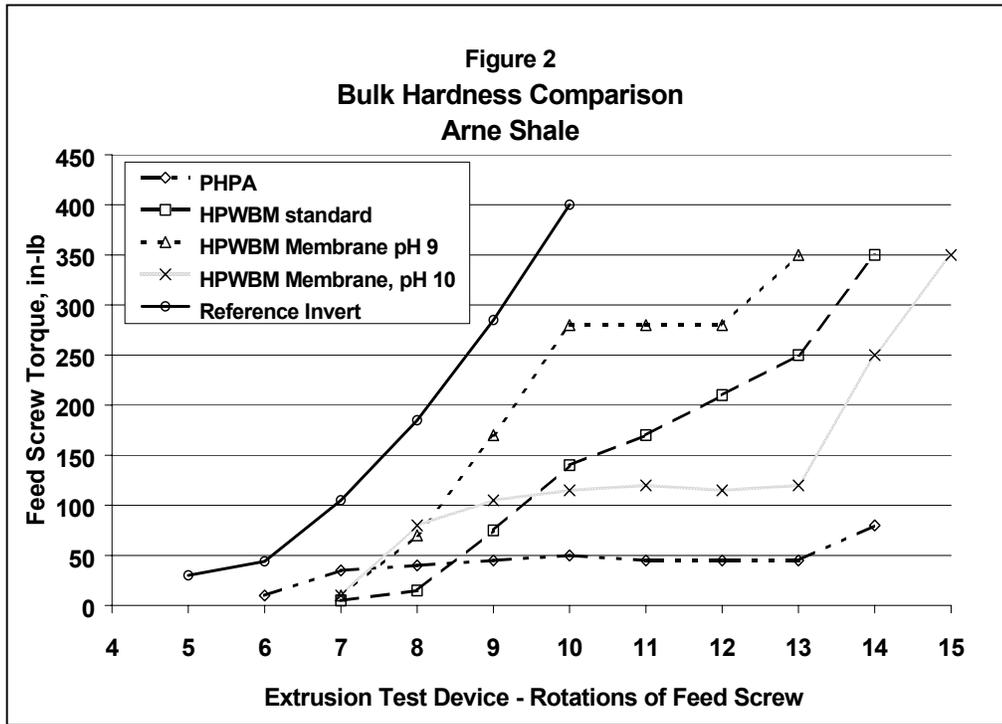
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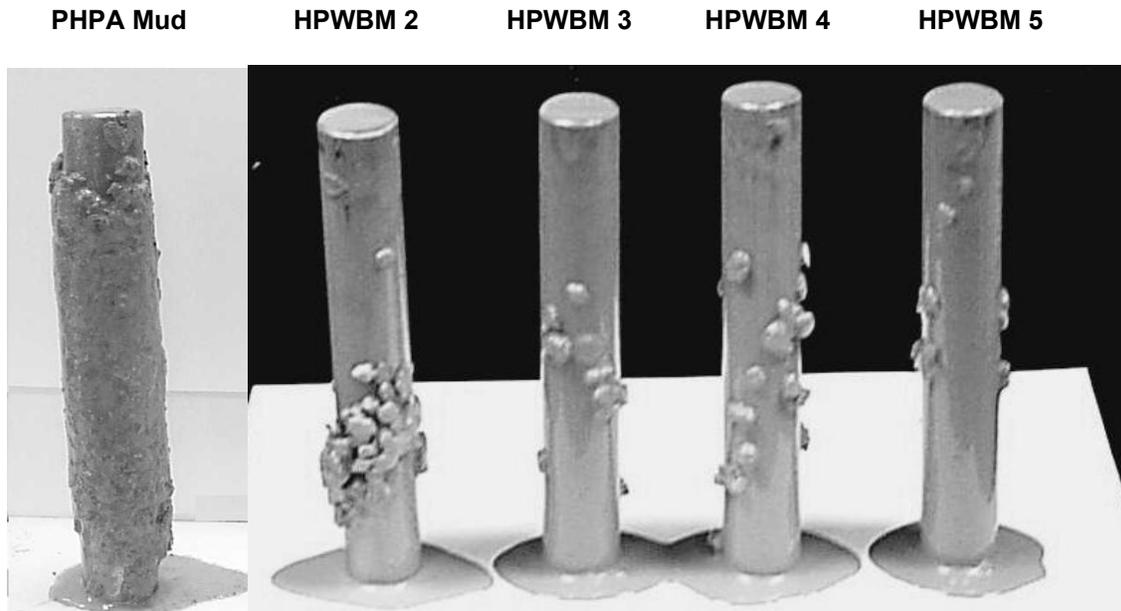
Table 1 – Mud Formulations						
	Units	PHPA-1	HPWBM-2	HPWBM-3	HPWBM-4	HPWBM-5
Type		no membrane	no membrane	membrane	membrane	membrane
freshwater (l)	ml		249	222	222	222
seawater (l)	ml	300				
PAC (s)	g	1				
prop cellulosic (s)	g		3.25	3.25	3.25	3.25
biopolymer (s)	g	0.5	1	1	1	1
cationic terpolymer (s)	g		1.5	1.5	1.5	1.5
PHPA A (s)	g	1				
PHPA B (s)	g	1				
bentonite (s)	g	6				
sodium chloride (s)	g	54.4	62.3	56.5	55	55
potassium chloride (s)	g	13.6				
ether amine (l)	g		10.5	10.5	17.5	17.5
antiret (l)	ml	10.5	10.5	10.5	10.5	10.5
barite (s)	g	161	184	187	187	187
rev dust (s)	g	25	25	25	25	25
initial pH adjustment	pH	8	8.5 - 9	8.5 - 9	8.5 - 9	8.5 - 9
Oligomer - membrane (s)	g			<b>25</b>	<b>25</b>	<b>25</b>
Adjust pH to	pH	8	8.5 - 9	8.5 - 9	to 10.5 AHR	to 10.5 BHR





<b>Table 2 – Test Details</b>	
<b>Hot Roll Stability Test</b>	
oven type	OFI 5 Roller Laboratory Oven
temperature	150°F (65.6°C)
time	16 hours
description of material	Field Cuttings - Gulf of Mexico
shale size	through 4 on 7 mesh
grams material	30 g
sieve screen used	20 Mesh (0.85 mm)
<b>Slaked Durability (Cage Test)</b>	
Rotation Speed	45 RPM
Temperature	ambient
Shale Type	Arne Shale
Shale Size	through 4 on 7 mesh
Test Screen Size	14 mesh
Rolling Abrasion Time	4 hours
grams material	30 g
<b>Bulk Hardness Test</b>	
pretreatment	Shale Rolled in Fluid of Interest
oven type	OFI 5 Roller Laboratory Oven
temperature	150°F (65.6°C)
time	16 hours
description of material	Arne Shale
shale size	through 4 on 7 mesh
grams material	35 g
sieve screen used	20 mesh
extruder plate	37 x 0.109 in (2.77 mm)
material extruded	30 g
<b>Accretion Test</b>	
oven type	OFI 5 Roller Laboratory Oven
temperature	80°F (26.6°C)
test duration	20 minutes
description of material	Arne outcrop shale
shale size	through 4 on 7 mesh
grams material	50 g
roller dimensions	23mm D x 150mm L (approx. 0.9 in D x 5.9 in L)
roller weight	475 g
material	P-110

**Figure 4 – Accretion Photos**



**Figure 5 - Polymer Solubility in 15% HCl**

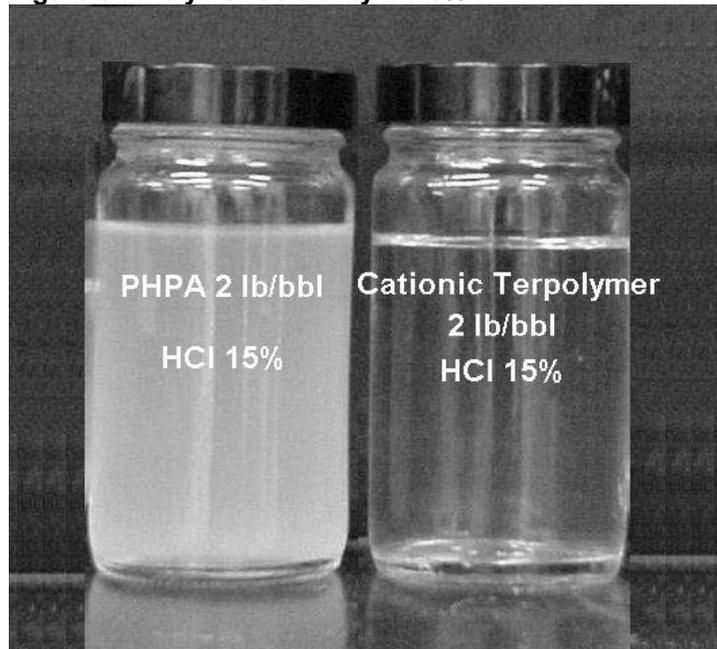


Figure 6 – Membrane and Shale Core

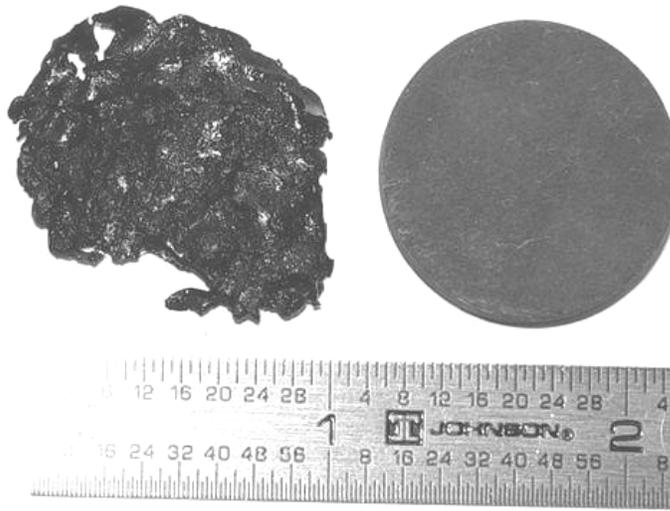


Figure 7

Shale Membrane Test - 072302rps  
 Cell 5 - HPWBM Membrane in NaCl 20%  
 on Preserved West African Shale

