

## Activated Proteinaceous Component of Uintaite Provides Clay Inhibition Properties. Case Histories

Katiuska Aguilar, Corey Webb, Ghery Sotomayor, and Ashley Reimann, American Gilsonite Company; Jason Nelson, Basin Fluids.

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### Abstract

The borehole instability associated with the reactivity of formation clay is one of the most severe and common issues encountered during drilling and completion operations when using WBM. The reactivity of water is controlled using inorganic salts and other organic cations. Recent studies indicate that the use of amino acids as clay inhibition agents has proven to be effective in controlling water activity on clay structural layers. The application of a non-conventional additive to reduce the impact of clay swelling was studied and applied at the field level in multiple wells drilled in various regions around the world. The proteinaceous composition found in the Uinta Basin was evaluated as an effective source of amino acids for clay inhibition, controlling the adverse chemical activity of clays. After activation of this pulverized material suspended in aqueous solution, wide inhibition tests were carried out using both bentonite and field clay samples, demonstrating the efficacy of this approach. The aqueous uintaite suspension has been used to drill 16,692+ feet with no evidence of hole instability. In benchmark wells wellbore instability problems were frequent, with problems including bit balling, difficulties during trip operations, torque and drag issues, among others. When the product was applied, dry drilling cuttings were observed with no signs of splintering or dumpy stickiness. The operational parameters were improved, achieving over five times better rheology values, 21% less torque, 27% ROP increase, and reducing casing runs by 3.5 hrs. All these improvements resulted in a mud cost reduction of 36 to 50% in the intermediate section.

### Introduction

To the layman, uintaite is a mineral. To the mineralogist, it is a mineraloid. But to the industrial chemist, it is a new material of primary importance in modern industry. Uintaite is an asphaltite found in commercial quantities only in Northeastern Utah in the Uinta Basin. (Crawford, 1942).

Uintaite originates from Kerogen type I, a kerogen of lacustrine origin, rich in lipid-derived aliphatic chains and has relatively low content of polynuclear aromatic systems and heteroatomic systems. Kerogen from the Green River formation

is rich in lipid material and contains predominantly aliphatic chains, with subordinate saturated cyclic material (Nciri et al. 2014, Hunt 1963, Sweeney, et al. 1987). An X-ray photoelectron analysis (ESCA) carried out by Helm et al in 2012 revealed that carbon was present mainly as aliphatic hydrocarbons. The study continued on to reveal that nitrogen-carbon bonding environments, such as aliphatic and aromatic amines, as well as nitrogen heterocycles such as pyrrole, the simplest five-membered unsaturated heterocyclic amine, were also present (Helm et al, McMurry, 2012 & 2023). The high nitrogen content indicates that proteinaceous material played an important part in the origin of uintaite and appears to have been derived largely, if not entirely, from plants. El Bourakadi et al., Trudeau and Hore (2019, 2010), explained from a molecular level viewpoint that the structural properties of some amino acids can repel water from invading the clay mineral by forming a hydrophobic layer around the mineral's surface, using their backbone hydrophobic properties. In other words, amino acids modify the clay surfaces hydrophobically which enables the clay surface to shield itself from invading water molecules. Muhammed, et al, (2021) refer that some amino acids show amphipathic nature due to their hydrophobic alkyl chain and charged head. Hence, they could form contacts with both polar and non-polar surface ligands simultaneously.

Uintaite is known as a superior performing additive used in both invert emulsions, as fluid loss control additive, and in water-based systems to assist in borehole stabilization and has been well documented over the years in case studies that this material works efficiently to minimize hole collapse in unstable shale sections. The unique natural combination and geochemistry of this material, with amphipathic characteristic available in meaningful quantities, makes uintaite a multifaceted mineraloid.

This paper discusses the chemistry of non-conventional, organic, nitrogen-based shale inhibitors; and illustrates how the natural chemical composition of uintaite accurately fits the characteristics of this new generation of shale inhibition materials.

From this extensive research, a novel combination of materials was designed to achieve efficient uintaite dispersion in aqueous environments through a chemical combination with biopolymers, enhancing the interaction of uintaite with shale layers while improving the rheological values in water-base systems.

The first novel uintaite suspension field application occurred 30 miles outside Casper, WY in the Powder River Basin, where water base systems are regularly used. The outcome in the first two wells where this novel uintaite suspension was applied is described in this paper, with significant drilling fluids performance optimization and moreover, operational parameters improvement.

The understanding of the geochemistry of uintaite led to the design of an effective and versatile additive, and the redefining

of this traditional and broadly recognized drilling fluid additive.

### Shale inhibition chemistry

Shale stabilization additives, crucial for preventing clay and shale reactions, in most cases require a combination of different types of shale inhibitors. The conventional inhibitors used in drilling fluids involve inorganic salts such as potassium chloride (KCl); though, sodium, ammonium, or calcium chloride are also commonly used. High concentrations of chlorine electrolytes in these inhibitors can lead to undesirable effects including flocculation, negatively impacting rheological properties, generating high fluid loss, thixotropy loss, and reducing cutting lifting capacity. Figure 1 describes a summary of different types of clay swelling inhibitors. The chart was built using research done by Muhammed, et al, (2021).

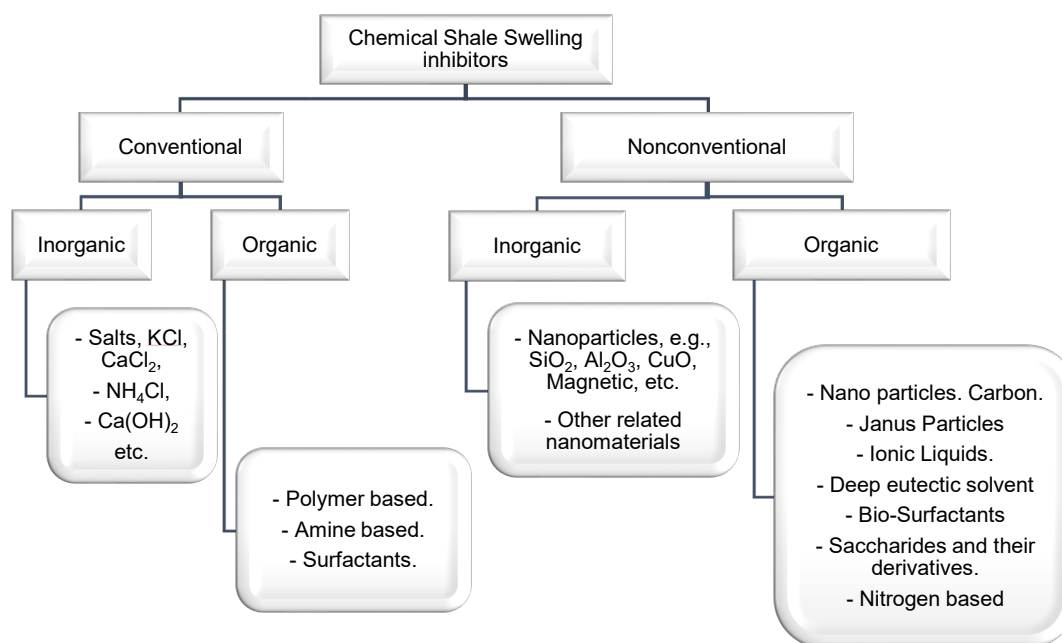


Figure 1. General classification of chemical shale swelling inhibitors.

Recent advancements in clay swelling inhibitors have developed alternative options that are environmentally friendly, cost-effective, offer improved thermal stability, have wide availability, and are overall more efficient. These materials include ionic liquids, organic nitrogen-based compounds, nanoparticles, Janus particles, biosurfactants, polysaccharides, and deep eutectic solvents. This paper focuses on non-conventional organic shale inhibitors, specifically those based on amines. See Figure 1. General classification of chemical shale swelling inhibitors.

To better understand shale inhibition chemistry, the next section of this paper compiles bibliographical references available on the topic.

### Nanoparticles

A variety of nanoparticles have been studied for enhancing the performance of rheological properties and shale inhibition of drilling muds, namely nano graphite, graphene oxide, carbon nano tubes, hydrophobic associated polymer-based nano-silica. Nanoparticles in drilling muds as a nanoscale additive can sustain HPHT and provide shale inhibition (Aftab, et al, 2017; (Mao, et al, 2015).

### Janus Particle

Another type of nanoparticle or microparticle named ‘Janus particle’, representing a unique group of patchy particles combining two or more different physical or chemical functionalities at their opposite sides. Especially, individual Janus particles with both chemical and geometrical anisotropy as well as their assembled layers, provide considerable advantages over the conventional monofunctional particles or surfactant molecules (Marschelke, et al, 2020). An example of a Janus particle is an amphiphilic graphene oxide, modified by dodecylamine on one side of graphene oxide: due to the amphiphilic structure, the hydrophilic side could spontaneously adsorb onto the clay surface, and the outward hydrophobic side could form a hydrophobic shield that impeded the interaction of clay and water (Lv, et al, 2020).

### Ionic Liquids

Ionic liquids (ILs) are characterized by combined ionic and covalent crystal structures with a higher organic cation percentage and relatively low anions existing as a liquid at room temperatures (Olayiwola et al., 2020). Khan et al, (2020) wrote recently that ionic liquids (ILs) have also been reported as clay swelling inhibitors. Ionic liquids are commonly defined as organic salts having a melting point under 100 °C. Rogers et al (2003) went on to explain that some cation groups of ILs are imidazolium, pyridinium, phosphonium, and ammonium, and some common anions are hexafluorophosphate, tetrafluoroborate, nitrate, octyl sulfate, chloride, bromide, and iodide. Several researchers have reported the performance of ILs on clay hydration and rheological properties. Figure 2 shows some ionic liquids structures.

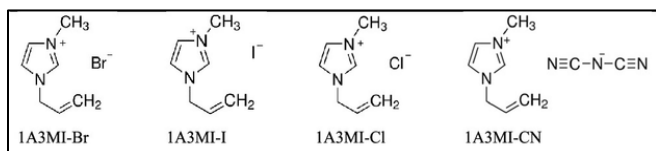


Figure 2. Structure of Ionic liquids

### Deep eutectic solvents

Deep eutectic solvents (DES) are the cheaper and greener alternative of ionic liquids and are generally composed of two or three components (Hydrogen Bond Acceptor and Hydrogen Bond Donors) which are capable of bonding with each other through hydrogen bonding to form a eutectic mixture at a particular temperature (Mecerreyes and Porcarelli, 2022). The eutectic mixture is the specific composition of at least two solid components that produces a change of phase to liquid at a certain temperature (Pena-Pereira and de la Calle, 2019). Rasool et al.(2022), mentioned in his paper that salts such as KCl are required in large quantity and are not environmentally friendly. Moreover, most polymers degrade at high temperatures, which renders them unsuitable for high-temperature high-pressure (HTHP) conditions during drilling. The quest of finding a cheaper and greener, but equally effective alternative for ionic liquids concluded with the

introduction of Deep Eutectic Solvent (DES) in drilling fluid. The usage of DES as a drilling fluid additive is still at its initial stages.

### Biosurfactants

Muhammed, et al, (2021) describe in their work that biosurfactants are surfactants derived from natural resources such as plant and animal extracts. Due to lower environmental footprints and biodegradability, these groups of surfactants have been reported to have the capability of combating shale swelling. The unique factor about these recently developed biosurfactants is their richness in saponin, which is a chemical compound. Quainoo et al (2020), explained that a typical saponin molecule contains both the hydrophilic and hydrophobic groups, which make them behave as a good surface acting agent. The hydrophilic group acts as an effective neutralizer on the clay surface through hydrogen bond formation, which limits the invasion of water during drilling and fracturing operations. Whereas the hydrophobic (water-repellent) group of the biosurfactants forms a strong hydrogen shield on or around the clay mineral surfaces, thereby limiting the close interaction between the water and the outer surface of the clay mineral.

### Saccharides and saccharide derivatives

The utilization of saccharides and their derivatives as effective clay stabilizers was considered due to the numerous hydroxyl ions available in their configurations. The hydroxyl groups of a commonly known saccharide – starch – can interact with the surface of clay minerals and, more importantly, with water via hydrogen bonding. Furthermore, saccharides are non-toxic and biodegradable, making them a likable natural material that can be easily disposed into the environment (Quainoo et al., 2020).

### Nitrogen Based

The effectiveness of amines in inhibiting clay swelling is well documented. Organic amine families, including nanoparticles and ionic liquids, play a crucial role in this context. Currently, different sources of organic amine families have been developed. Some nanoparticles and ionic liquids shale inhibitors are based on organic nitrogen. Muhammed, et al (2021), collected literature on nitrogen-based inhibitors such as Gelatin, Polyethyleneimine, Oligo Poly L-Lysine, Cycloaliphatic amine Dopamine Bis (hexamethylene) triamine, Poly (oxypropylene)-amidoamine, and Gelatin Quaternary Ammonium Salts.

Poly (oxypropylene)-amidoamine (POAA), as a new counteractive agent, was examined by Zhong (2012) as an effective clay stabilizer. Y. Liu et al. (2021) developed a type of hyperbranched polymer with a higher ratio of amine groups. Benefiting from this molecular structure with primary and secondary amines and amide groups, protonated products in alkaline drilling fluids endow the molecule with strong absorbability and thus help boost the inhibition performance.

Xuan et al. (2015) and Li et al. (2020) investigated the use of Oligo Poly L-Lysine, and Poly L-Arginine (polymers of amino acids) as effective clay stabilizers possessing superior stabilizing potential over KCl. However, these amine-based chemicals are challenged with cost and high molecular weights.

Amino acids are naturally occurring biomolecules that combine to form proteins. They consist of amine ( $-\text{NH}_2$ ) and carboxylic acid ( $-\text{COOH}$ ) functional groups and unique sidechains whose specificity (nature and arrangement) determines their physical and chemical properties (Bavoh et al., 2017; Madeira et al., 2014; Vyas and Ojha, 2010; Xu et al., 2003). Amino acids can be considered as potential clay swelling inhibitors due to several reasons. Firstly, amino acids exhibit zwitterionic properties in aqueous environments, enabling the protonation of their amine groups into ammonium ions within a given pH range. The protonated groups then form hydrogen bonds with water (Sa et al., 2016). The induced bonds aid in the reduction and disruption of water molecules away from the clay mineral, resulting in the significant reduction of clay swelling. Secondly, amino acids are amphiphilic compounds. This is noticed in their hydrophilic and hydrophobic ends. Some amino acids show amphipathic nature due to their hydrophobic alkyl chain and charged head. Hence, they could form contacts with both polar and non-polar surface ligands simultaneously. (Muhammed, et al, 2021). Overall, the mechanism of inhibition is achieved via (1) surface adsorption on the active clay minerals with their protonated ions to form a hydrogen bond capable of repelling water encroachment and (2) through the formation of a strong hydrophobic shield around the active clay minerals (Kommareddy et al., 2007).

It should be noted that, as discussed in the introduction section of this paper the chemistry of uintaite also shares commonalities with the above amino acid descriptions due to its high nitrogen content, originated from proteinaceous material. This topic is delineated in detail in the following section of this paper.

### Gilsonite Uintaite Chemistry

The nitrogen content in the chemical structure of uintaite is defined by the presence of porphyrin, which was isolated in the form of a crystalline porphyrin by Sugihara and McGee (1957). Porphyrins are a class of macrocycles comprised of four pyrrole units conjugated through methine bridges (Bryden, and Boyle, 2016). Figure 3 represents the porphyrins chemical structure from McGee's studies. Knowledge of types of porphyrins in asphaltic materials can provide useful information in interpreting their origin and mode of formation. The predominance of decarboxylated porphyrins indicates that the temperature range involved in the formation of this bitumen was, at one time, not less than 250° to 350°F. Temperatures appreciably more than 400°F could not have been involved, since porphyrins undergo degradation at such temperatures (McGee 1956).

Katritzky, et al, (2010, 2023), explain in their book that Pyrrole rings are found in the amino acids proline and hydroxyproline, and in colored natural products, such as chlorophyll, heme (a part of hemoglobin), which are components of many proteins and which are present in particularly high concentrations in collagen, the structural protein. Pyrrole derivatives are widespread in the living world and the p compounds are found among the alkaloids, a large class of alkaline organic nitrogen compounds produced primarily by plants. McGee (1956) concludes that the high nitrogen content indicates that proteinaceous material played an important part in the origin of uintaite.

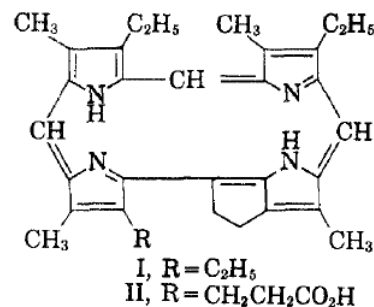


Figure 3. Porphyrins chemical structure (Sugihara and McGee, 1957)

In 2014, Nciri et al. performed a uintaite characterization by elemental analysis (EA) to determine the concentrations of C, H, N, S, and O, by Fourier Transform Infrared Spectroscopy (FTIR) for comparative analysis of the chemical structures, by Nuclear Magnetic Resonance spectroscopy of hydrogen ( $^1\text{H}$  NMR) to ascertain the aliphatic and aromatic hydrogen fractions, and by Thin Layer Chromatography-flame Ionization Detection (Iatroscan TLC-FID) to quantify saturated and aromatic hydrocarbons and resin/asphaltene fractions. The results were evaluated in combination with the available geological data and with some bitumens to evaluate, chemically, possible mechanisms of uintaite formation. The uintaite in their study can be related geochemically to the oil shale kerogen from the Green River formation. The elemental analysis indicated noticeably that carbon (84.36 wt.%), and some amounts of hydrogen (10.05 wt.%) predominantly compose uintaite. The content of oxygen (1.36 wt.%) and sulfur (0.27 wt.%) was quite small. However, the nitrogen content was significantly high (3.25 wt.%). Those results are summarized in Table 1.

As cited previously, nitrogen is derived mainly from proteinaceous material, which is destroyed rapidly during diagenesis. Most high-nitrogen kerogens were therefore deposited under anoxic conditions where diagenesis was severely limited (Nciri et al. 2014).

Table 1. Properties of Bitumens (Nciri et al. 2014)

Property	Bitumen			
	Uintaite	TLA	Petroleum pitch	Oil shale kerogen
Carbon, wt. %	84.36	50.38	84.44	80.5
Hydrogen, wt. %	10.05	6.06	9.19	10.3
<b>Nitrogen, wt. %</b>	<b>3.25</b>	0.72	0.43	2.4
Sulfur, wt. %	0.27	4.14	5.69	1
Oxygen, wt. %	1.36	4.71	3.24	5.8
H/C, atomic ratio	1.44	1.44	1.31	1.53
O/C, atomic ratio	0.01	0.07	0.02	0.05
C/N, atomic ratio	39.05	104.75	305.65	50.37
S/C, atomic ratio	0.01	0.03	0.02	0.04
Heating value (Btu/Lb)	17,812	10,627	17,421	17,080
<b>Organic matter, wt. %</b>	<b>99.32</b>	66.01	100	100
Inorganic matter, wt. %	0.68	33.99	0	0

In Table 1, the chemical analysis shows that the organic matter of uintaite is 99.32%<sup>wt</sup>, consequently most of the nitrogen content is also organic in nature.

When Electron Spectroscopy for Chemical Applications (ESCA) and X-ray Photoelectron Spectroscopy (XPS) was employed by Clark et al. (1983), the results indicated that carbon in uintaite was present as aliphatic hydrocarbons, nitrogen-carbon bonding environments, such as aliphatic and aromatic amines, as well as nitrogen heterocycles such as pyrrole were present; and that C-O bonding environments were present, with very small amounts of sulfur as organic sulfides or heterocycles such as thiophenes.

Helm et al, (2012) investigated the composition and structure of uintaite with different analytical techniques, such as NMR, ESI-FT-ICR-MS. Aromatic moieties in uintaite were primarily single rings or small clusters of fused rings. Half of the aromatic carbons of uintaite can be accounted for by pyrroles. Isotopes of <sup>15</sup>N and <sup>13</sup>C cross polarization-magic angle spinning (CP-MAS) NMR showed that most nitrogen in uintaite was pyrrolic.

Figure 4, (a) shows the <sup>15</sup>N CP/MAS spectrum of uintaite without dipolar dephasing, while (b) shows 291 $\mu$ s recoupled <sup>1</sup>H-<sup>15</sup>N dipolar dephasing, which suppresses the signals of protonated nitrogen. No significant signals were detected in the <sup>15</sup>N CP/MAS with recoupled dipolar dephasing (b), indicating that all N forms are protonated, consistent with pyrrolic N-H groups (Helm et al, 2012).

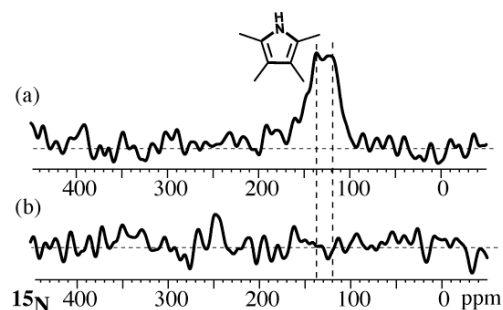


Figure 4. <sup>15</sup>N and <sup>13</sup>C cross polarization-magic angle spinning (CP-MAS) NMR of uintaite. (Helm et al, 2012)

### Pyrrole rings analysis

Aromatic carbons in uintaite were either part of five membered (pyrrole) or "regular" six membered aromatic rings. Based on the C/N ratio and the aromatic carbon fraction determined by quantitative <sup>13</sup>C NMR, we determined an upper limit to the abundance of pyrrole rings. Therefore, the pyrrolic carbons accounted for 2 x 7% = 14% of all C, and other aromatics for 27 - 14 = 13%. Further, 14% C in pyrrole rings corresponded to 14/4 = 3.5 N per 100 C. This means that nearly all the N was in pyrrole rings (Helm et al. 2012).

By combining the information obtained from advanced NMR and ultrahigh resolution MS, Helms et al, (2012) proposed a structural model for uintaite as a mixture of many pyrrolic and a few fused aromatic rings highly substituted with and connected by mobile aliphatic chains. See Figure 5.



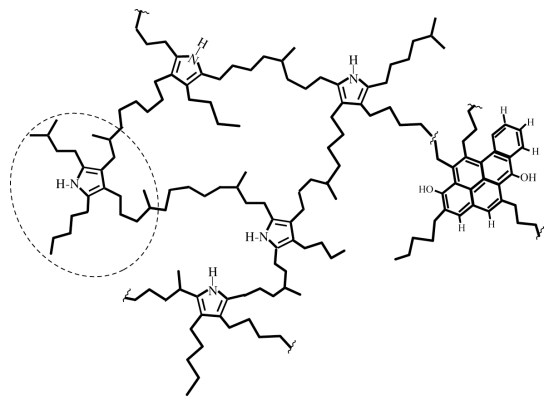


Figure 5. Model of the main components of uintaite. (Helm et al, 2012)

In his study, Helm (2012) provided a schematic of a typical uintaite monomer unit and highlighted the unit with a stashed ellipse, which contains one aromatic ring and 21 carbons.

In 2020 Bishop et al, in their specialized laboratory in Houston, Texas performed a comprehensive geochemistry analysis with 3 sources of foreign asphaltites compared with uintaite (sample C in Table 2 below). The results show several differences in the chemistry and geochemistry characteristics. For purposes of this study, only the nitrogen-related results are shown.

Table 2. Bulk fraction compositional data, combining total asphaltene contents with SARA fractionation results Source: Bishop et al, 2020

Asphaltites	‰ $\delta^{13}\text{C}$ Carbon	‰ $\delta^{15}\text{N}$ Nitrogen	‰ $\delta\text{D}$ Hydrogen	‰ $\delta^{34}\text{S}$ Sulfur
A	-27.3	2.6	-106	7.5
B	-36.0	2.7	-99	11.4
C (uintaite)	-29.5	17.0	-186	26.3
D	-29.0	-0.1	-89	-11.3

Bulk isotope data was measured on the heptane precipitated asphaltenes for carbon, hydrogen, sulfur, and nitrogen. The results are shown in Table 2, and plotted in a series of charts in Figure 6. All the isotopes show considerable variation between the samples. However, sample C appears to be more distinct than the others. It has markedly different sulfur, hydrogen, and nitrogen isotopic compositions (Bishop, 2020).

Figure 6 shows the  $\delta^{15}\text{N}$  nitrogen isotope versus  $\delta^{34}\text{S}$  sulfur and  $\delta\text{D}$  hydrogen. All the samples are markedly different in terms of their carbon and sulfur isotopic compositions, but only sample C (uintaite) has pronounced differences in the hydrogen and nitrogen isotopes.

These analyses clearly show how the unique chemistry of uintaite works and explain its effectiveness as a swelling inhibitor based on its organic nitrogen content. Uintaite geochemistry fits that of non-conventional organic shale inhibitors, which is based on amines of amphipathic nature, where the hydrophilic side reacts with negative charges on clay surfaces and the hydrophobic side of the hydrogen bridges forms bonding links to prevent clay reactions, creating a shield around the clay minerals that repels water. This mechanism is represented in Figure 7.

Utilizing the chemical principles outlined above, a novel combination of materials was designed to allow for efficient uintaite dispersion in aqueous environments through a chemical combination with biopolymers, enhancing the interaction of uintaite with shale layers. The secondary benefits of this novel blend, besides activating the functional groups for shale inhibition in uintaite, include low shear rate viscosity (LSRV) enhancement, and lubricity coefficient reduction, thus avoiding the requirement for additional mud additives.

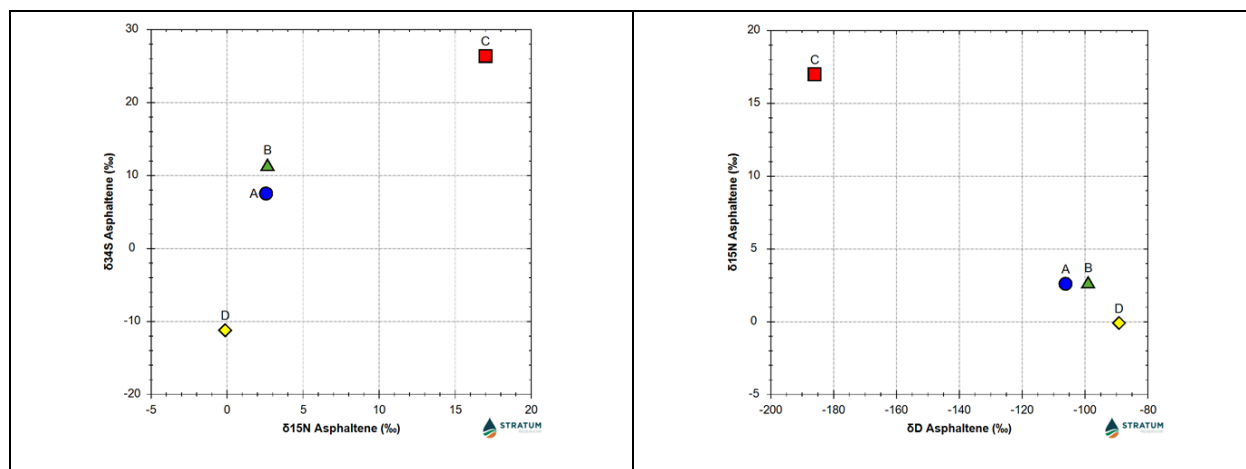


Figure 6. Selection of cross-plots for the isotopes measured on the heptane insoluble asphaltene fraction for each sample. (Bishop, 2020)

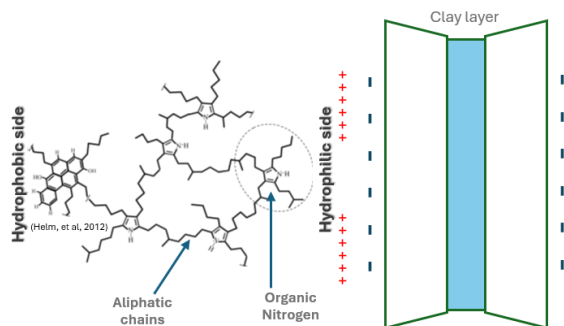


Figure 7. Representation of uintaite geochemical hydrophilic/hydrophobic functional groups

This novel uintaite suspension in aqueous media constitutes a step forward when it comes to understanding and enabling the geochemistry of uintaite in drilling fluids applications. To provide context on uintaite's long history and knowledge of the industry in WBM applications, select field application examples are described in the next section.

### Case Histories, Field Data

Uintaite has been historically used as a shale control additive in WBM's with well documented success. This work compiles some of the most documented cases histories until now, to provide context on the progress and evolution of uintaite applications in water-based drilling fluids systems.

#### A Look to the past,

In the past, many experiences have been documented with a noticeable shale stabilization performance when uintaite was used in Water Based Muds (WBM) formulations. Different types of dispersion processes were implemented to get uintaite homogenized in the mud, because its specific gravity is very close to water (1.01-1.04) so it tends to float on the fluid's surface. Nonetheless, when uintaite was used, shale stabilization in the wellbore was noted.

During the Hackberry field campaign in Louisiana, 14 wells were drilled with uintaite as stabilizer used to deal with water sensitive sloughing shales. Before this change, weighing up was commonly used to control well stability, but this resulted in low ROP, high mud cost, occasional differential sticking, and high total well cost. A polymer mud had been used and it was gradually converted to a dispersed lignosulfonates mud. For those wells, more than 160,000 ft were drilled, the mud density ranged as low as 10.5 ppg and 12.8 ppg was the highest without serious shale problems, stuck pipe or lost hole occurring. The sloughing tendency in the normally pressured shales is caused by weakening due to mud filtrate invasion, where the uintaite retards filtrate invasion into the formation and along bedding planes and microfractures. Some caliper logs showed gauge holes when uintaite was initially added (Cagle, 1972). Caliper logs are shown in Figure 8.

Continuing the early research done in previous decades, in the 1980's ample research was carried out to understand potential benefits of uintaite in WBM's. Many blends of uintaite and other additives were evaluated and tried in the field – below are some applications of such blends, which included uintaite with different surfactants and materials, and the outcome is described below.

In the South Pass area offshore Louisiana, a blended uintaite material and surfactant were used to reduce torque and drag in a well. Wells in this area normally are deviated approximately 30° from vertical and are drilled with conventional lignosulfonate mud. On Well A, conventional and bead-type lubricants had been used for torque and drag reduction. On Well B, 3-lbm/bbl. [8.56-kg/m<sup>3</sup>] of uintaite was added at approximately 10,600ft [3231-m] measured depth. By comparison with Well A, torque on Well B was reduced on an average from 1,400 to 900 ft-lbf [1897 to 1220 J], a 36% reduction; and drag was reduced on an average from 60,000 to 30,000 lbf [27220 to 13 600 kg], a 50% reduction. Caliper-log comparisons from these two wells indicate substantial improvement on Well B (Davis, & Tooman, 1989).

Another well was drilled in the Eugene Island area of offshore Louisiana. While this area is not known for borehole instability, hole enlargement, however, is a problem. Prior to the introduction of blended uintaite product, hole enlargement averaged about 50% in the 12.25-inch hole. At casing point, 4 ppb of uintaite, suspended in a water-based solution, were added to a conventional water-based solution. Hole enlargement in the 8-½ inch hole was reduced to an average of 15% (Davis, & Tooman, 1989).

In 1987 Chevron conducted an experiment to obtain data which could be used to comparatively evaluate the ability of various mud systems to stabilize highly reactive shales and gumbos, such as those found in the U. S. Gulf Coast. The mud systems used in this study range from the commonly used chrome lignosulfonate system to polymer systems to variations of gypsum or lime systems. To evaluate the ability of the various mud systems to stabilize the borehole, four-arm or six-arm caliper logs were run in intervals of interest. The average borehole diameter was calculated from this caliper data. The results were consistent with the findings of independent work performed at the same time. The commonly used chrome-lignosulfonate mud had the highest amount of washout (139 - 179%). The mud containing only potassium hydroxide provided a hole with washout reduced to 0 - 10%. The other mud systems provided borehole with washouts ranging between 14 - 116%. The use of uintaite as a shale stabilizer in the wells in this experiment varied. An attempt to obtain correlating control based upon the use of uintaite was not made; however, some qualitative observations can be reached after studying the data. Well #3 used uintaite and had almost no washout; the observed washout values were -7% and 12% for the respective hole sections. The negative number was caused

by the calipers being slightly out of calibration. The actual washout on this section was on the order of 0 to 10%. The calculated washouts on Well #8, where uintaite was not used, were 15% and 38%. If the assumptions stated above are applicable, the main difference between these two systems was the use of uintaite, and the observed changes in washout would be consistent with reductions in washouts attributed to uintaite as documented by Davis, & Tooman, 1989. Caliper logs are showed in Figure 8 (Gilmore & Sanclemente, 1989).

A few decades later in a Chevron drilling campaign in the Gulf of Mexico, a new blended material was tried, Davis & Gilbreath (2002) applying a strong surfactant to coat uintaites with different softening points; additionally a deflocculant was added for better dispersibility in the mud system. The mud system was lignite/polymer and was initially treated with 2 ppb of the product and maintained with 2-5 ppb. The well was successful, reaching the total depth of 8400 ft. with no problems. Hole angle averaged 21 degrees; mud weights ranged from 9.7 to 10.7 pounds per gallon (ppg). No excessive torque or drag was encountered. Caliper logs in the open hole interval showed washout averaging 16% while surrounding wells without the coated blended material experienced 30-40% washouts. Additional tests in the Gulf and in other areas were conducted using various other water-based mud systems and similar results were achieved. Older aged shales such as the ones found in the Rocky Mountains and Canada indicated even lower hole washout.

The results of wellbore stability observed in the wells drilled by Chevron in the Gulf of Mexico showed that the test simulation conducted with the Downhole Simulation Cell (DSC) apparatus correlated. Part of the results of this study is shown in Figure 9, where the washout differentiation is evident when uintaite is used.

On another well, in Evanston, Wyoming, borehole instability was encountered, a common occurrence in this basin. The shale sections are hard and brittle, mostly Cretaceous or older in age. The area is in the thrust fault zone known as the Hinge Line. On this well, excessive torque and drag, bridges after trips, and reaming problems continued to increase. An inhibitive, KOH gypsum mud system was being used and some chemical alteration was observed from the cuttings. An on-site analysis suggested that tectonic stress was the probable cause of borehole instability problems. A hole cleaning program was initiated by first viscosifying the mud by increasing the YP from 7 to 15 lbs/ft<sup>2</sup>. Secondly, 5 ppb of the blended uintaite material was added to the system. Torque and drag was reduced

substantially. Bridging and reaming after trips were no longer encountered. Within two days, hole stabilization was achieved, and drilling continued without further instability issues. On other wells drilled in troublesome shale areas, mainly in the older shale rocks, blended uintaite in concentrations of 5-6 ppb have been used in various mud systems, including polymer muds and salt treated systems. The problems caused by shale were substantially reduced (Davis, & Gillbreath, 2002).

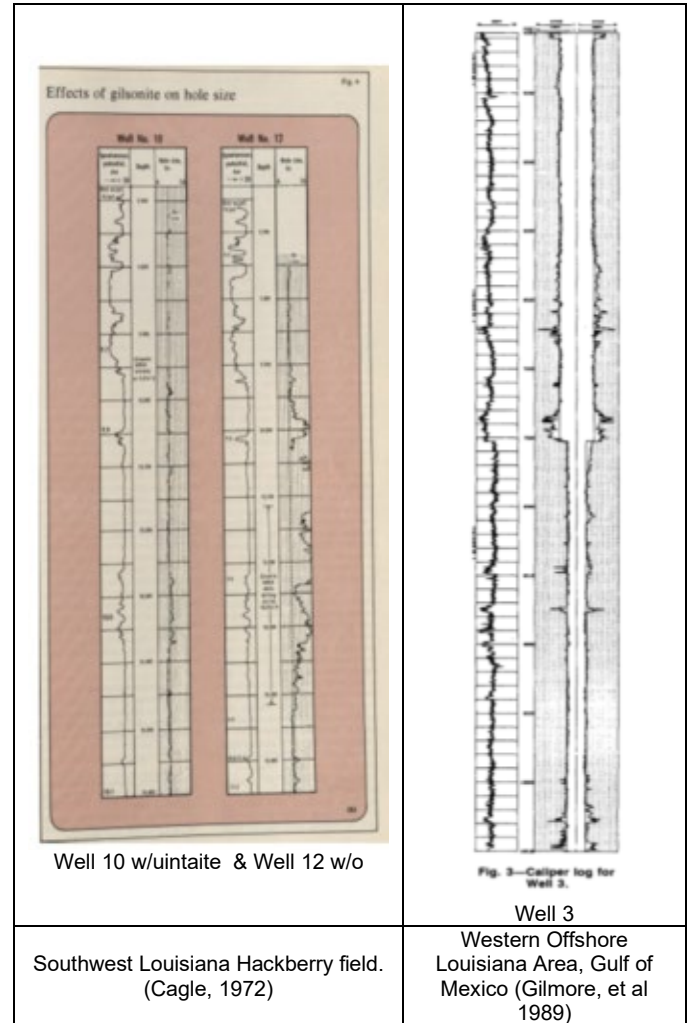


Figure 8. Representation of uintaite geochemical hydrophilic/hydrophobic functional groups



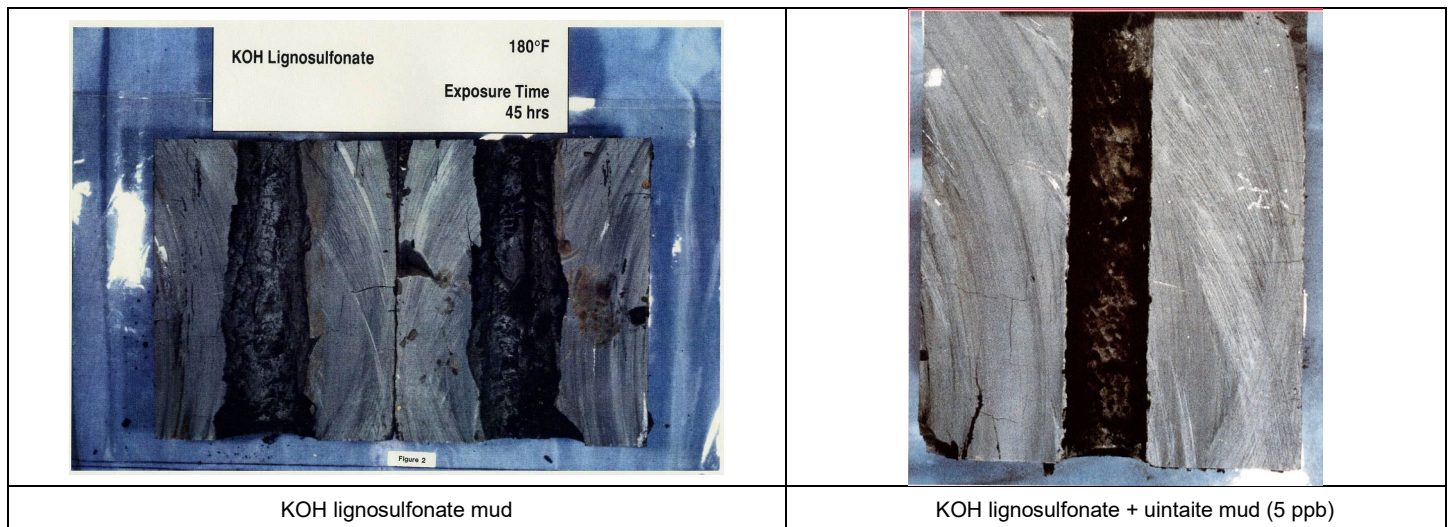


Figure 9. Downhole Simulation Cell (DSC) apparatus results of Pierre shale drilled after 45 hours exposure at 180°F. (Davis, & Gillbreath, 2002).

### Novel Aqueous Uintaite Suspension Development

The development of aqueous uintaite dispersion is based on chemistry, allowing individual particle reaction instead of clustering. The cationic compounds interact seamlessly with the slight polarity of the biopolymers contained in the novel blend. SEM images illustrate the difference between untreated uintaite and uintaite suspension, showing improved dispersion in water-based fluids.

Figure 10 shows the differences between untreated uintaite (a) non miscible when added directly to water. (b) while the novel liquid uintaite suspension is fully dispersible in water. The product is easily added to WBM's (c).

A Scanning Electron Microscopy (SEM) was used to observe how the novel combination of uintaite and biopolymers look at a micro-level. In Figure 11 (a) it is possible to observe that untreated uintaite particles tend to cluster in the WBM due to its hydrophobic nature; further, because of its low density (1.02 – 1.04 sg) it also floats on top; however in (b) the drilling mud looks homogeneous when the novel aqueous uintaite suspension is used. SEM images of the filter cakes formed by the WBM were taken. In (c) one cluster of untreated uintaite particles is measured at 125 $\mu$ , while the image (d) of the novel uintaite suspension has an average particle size of 48 $\mu$ , which is the actual size of the pulverized uintaite, indicating that full dispersion is achieved.

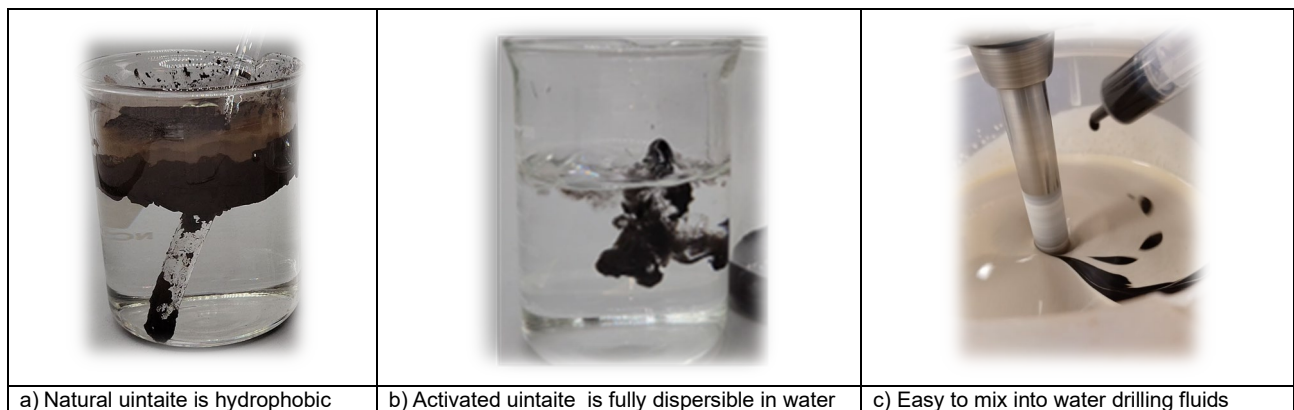


Figure 10. Dispersion of novel liquid uintaite suspension

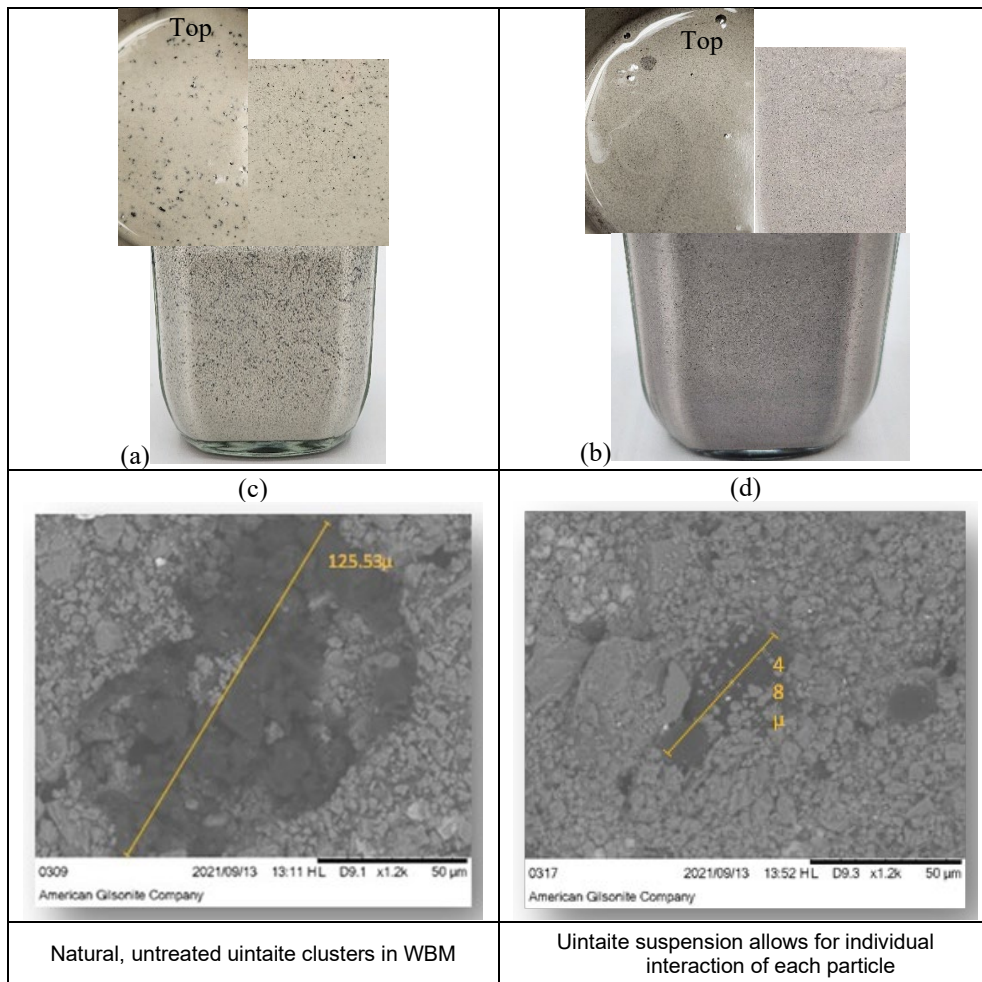


Figure 11. Comparison between WBM's prepared with untreated uintaite and uintaite suspension

The particle dispersion effect was also observed on the mud cake generated after carrying out the API fluid loss test in

comparison with the known liquid uintaite glycol based and surfactant treated uintaite, see Figure 12.



Figure 12. Filter cakes photos after the API fluid loss test

**Novel uintaite suspension Field Application**

The first novel uintaite suspension field application occurred 30 miles outside Casper, WY in the Powder River Basin, where water base systems are regularly applied with different levels of success. The next section discusses the comprehensive lab tests carried out before and during the field

trial of this novel product to document and understand its performance.

**Lab Testing**

Comprehensive lab evaluations before and during drilling operations highlight the rheological and low shear rate viscosity

performance, lubricity properties, and shale inhibition of the uintaite suspension. The formulation significantly improves rheology properties and reduces torque and drag.

### Rheology and low shear rate viscosity performance tests

The biopolymers, a key component in the novel uintaite suspension formulation, have thixotropic behavior. This property generates solids arrangement not only within the aqueous uintaite suspension, but also in the drilling mud. For instance, the LSRV value in the lab formulation containing the novel product was five (5) times higher than in the blank formulation. In the actual field application, the rheology properties were improved by 6.5 times on average as described in Table 3. See Figure 13.

### Lubricity coefficient test

Lubricity properties were evaluated with a Metal-to-Metal Lubricity test using a model EP-Lubricity tester; two WBM formulations were prepared and aged to 250°F, one was a blank and the other with 2%v/v of the liquid uintaite suspension added. The result was a reduction of 26.08% in the lubricity coefficient (see Table 3 and Figure 13). An equivalent outcome was observed in the wells drilled with a 21% reduction in torque and drag versus benchmark wells.

Table 3. Rheology Properties of the WBM formulations used to test the novel uintaite suspension. Lab formulation after aging at 250°F

Properties	Blank	Uintaite suspension
Plastic Viscosity (cP)	13.3	16
Yield Point (lbs/100ft <sup>2</sup> )	16.7	24.8
Gels 10" (lbs/100ft <sup>2</sup> )	3.5	7.1
Gels 10' (lbs/100ft <sup>2</sup> )	5.4	12.7
R-6	5	10.7
R-3	3.5	7.5
LSRV, 0.3 rpm	3600	17730
Lubricity coefficient	0.36	0.26
% Lubricity Reduction	-	26.08

### Shale inhibition

Rolling Bar Test Method and Dynamic Linear Swell Meter tests conducted using sodium bentonite pellets and field cuttings samples demonstrate the clay inhibition capabilities of the novel uintaite suspension.

The method employed was a compilation of Van Oort, Eric, et al (2015) and S. Cliffe, and S. Young. (2008) with one laboratory barrel (350 ml) of the drilling fluid formulation under study, compared with a blank formulation. The procedure is described below:

1. Place a clean solid steel bar in an aging cell containing drilling fluid.

2. Add 25 grams (W1) of shale cuttings to the cell or 1/4" bentonite pellets, equilibrated to a water activity  $a_w$  shale = 1.0, used to simulate the effect of reactive shale cuttings.
3. Seal the lid of the cell and place it horizontally in a roller oven at 120 °F for 30 minutes.
4. Carefully remove the bar from the cell and gently rinse off any extra mud.

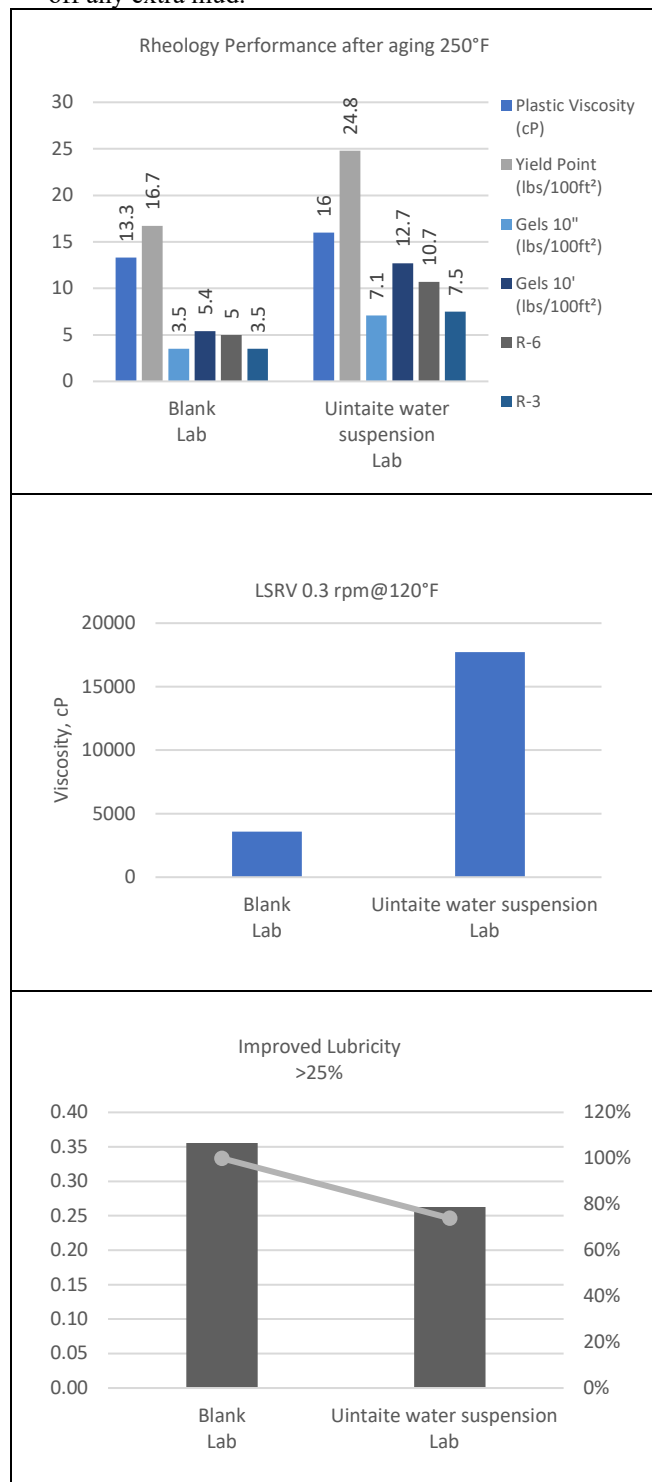


Figure 13. Performance effects on rheology, LSRV, and lubricity when the novel aqueous uintaite suspension is used compared to a blank formulation.



5. Scrape off adhered solids from the steel bar and measure its weight (W2).

6. Allow the accreted solids to dry to a constant weight (W3) at 220 °F. Quantitatively, the percentage accretion was calculated from the dry weight of accreted solids using the following relation:

$$\% \text{ Accretion} = \frac{W_3}{[(100 - M_i)/100] \times W_1}$$

The results showcase a reduction in percentage accretion and swelling, confirming its effectiveness in preventing clay reactions. See results in Table 4.

A field clay sample was taken at 2,500ft of a shallow well and evaluated with a Dynamic Linear Swell Meter. Two clay wafers were compacted and placed to soak for 24 hr., one wafer was soaked in tap water and the other in a WBM formulated with 2% of the novel uintaite suspension. A notable 54% swelling reduction was observed during this test. The results are shown in Table 4. (See Figures 14 and 15).

Table 4. Shale inhibition results

Evaluated fluid	Clay sample	% Shale Accretion	% Clay swelling
WBM + uintaite water suspension	Bentonite pellets	2.1%	-
Blank	Bentonite pellets	67.2%	-
WBM + uintaite water suspension	field clay	1.3%	-
Blank	field clay	15.8%	-
WBM + uintaite water suspension	field clay	-	22.8%
Tap Water	field clay	-	42.6%

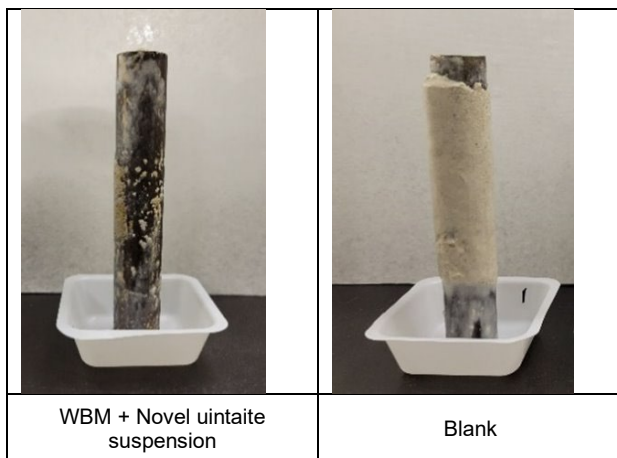


Figure 14. Accretion test results with sodium bentonite pellets

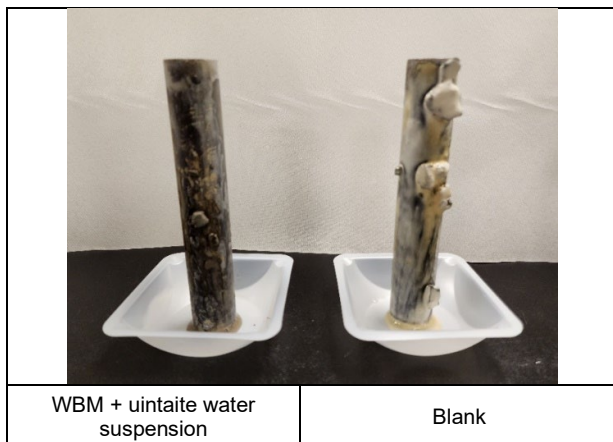


Figure 15. Accretion test results with field samples

### Case History of uintaite water suspension

In the Rockies Powder River Basin, two wells were drilled using the novel uintaite suspension designed to improve its dispersion in water-based systems. The 8.75” intermediate sections were drilled from ~2,950 to ~11,300 ft utilizing a potassium chloride-based polymer drilling fluid supplemented with the novel uintaite suspension for added inhibition and wellbore stability.

The novel liquid uintaite water-based suspension was added to the first well at ~4000 ft and the effect over the system was notable. Once additions of the novel uintaite suspension were made, it was observed that the API Filtrate improved with each 12-hour tour. Once additions commenced, the API was measured at 18 mL/30 min on the first day and was reduced to as low as 11mL/30 min. Notwithstanding the high concentration of calcium additions used to combat the CO<sub>2</sub> contamination posed an additional challenge while drilling the last 3,000 ft. High hardness/calcium levels typically have a negative impact on the effectiveness of filtration control polymers used to reduce API filtrate. The intermediate hole was finished with an API of 12 mL/30 min while fighting the CO<sub>2</sub> all the way until TD at 11,330 ft. In addition, torque also improved slightly from the high of 28 to 22 kf-lbf per the directional driller. At TD while the wellbore was being circulated clean, the characteristics of the cuttings observed coming across the shakers were well defined, no splintering, nor swelling/hydration, indicating optimal inhibition and wellbore integrity. Wiper trip operation took a total of 8 hours from end of well, back to the shoe of the surface casing and back. Additionally, an improvement of GPM (gallons per minute) was observed on the wells in which the uintaite was used, allowing for increased hole-cleaning efficiency. In comparing drilling conditions between the previous well’s intermediate



intervals and the wells where this suspension product was used, the ROP average improved by 27%. Rheological properties are reported in Table 5.

For the second well there was a focused effort to reduce additions of other wellbore strengthening agents and utilize the uintaite suspension. After a successful first field trial yielded intermediate section cost savings of 36%, the decision was made to run a second trial. In the second trial, total fluid additive volumes were reduced, including sulfonated asphalt and xanthan gum, resulting in intermediate section mud cost

reduction of 50%. Half of sulfonated asphalt was reduced in the second well on the last 4,500 ft of the well and the API filtrate and cake improved immensely despite the CO<sub>2</sub> contamination in the WBM system. After back at bottom, the hole was circulated clean and while tripping out of the newly drilled wellbore there was no hole instability or tight hole issues encountered. The Intermediate 7" casing run took about 13 hours with no issues – 3.5 hours less than planned/usual. A typical well design is shown in Figure 16.

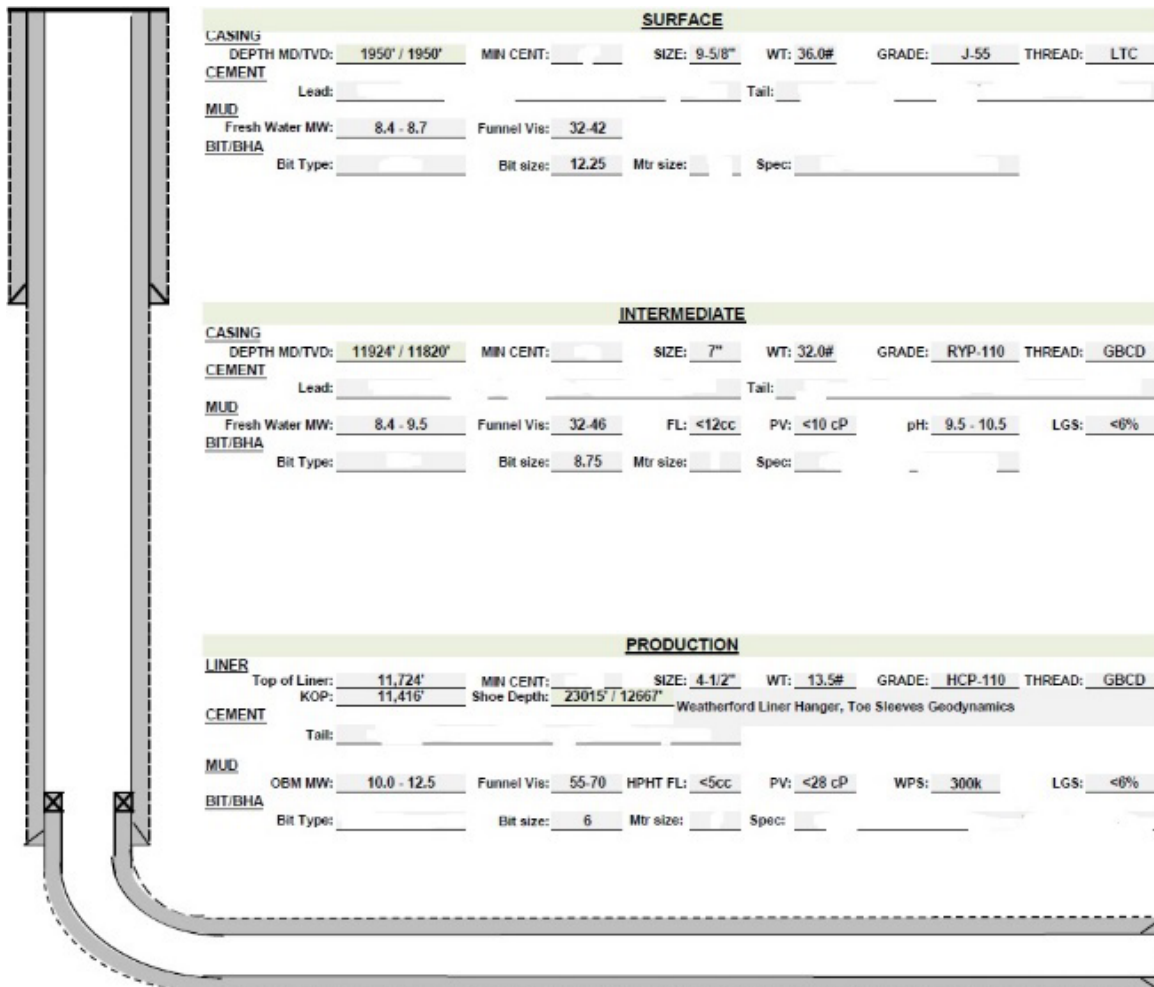


Figure 16. Typical well design for the Powder River Basin

Table 5. Rheological properties during drilling operations with the novel uintaite suspension

Properties	Field samples (160°F)	
	Wells - before	Wells -after
Plastic Viscosity (cP)	1	7
Yield Point (lbs/100ft <sup>2</sup> )	3	16
Gels 10" (lbs/100ft <sup>2</sup> )	2	8
Gels 10' (lbs/100ft <sup>2</sup> )	2	15
R-6	1	8
R-3	1	7

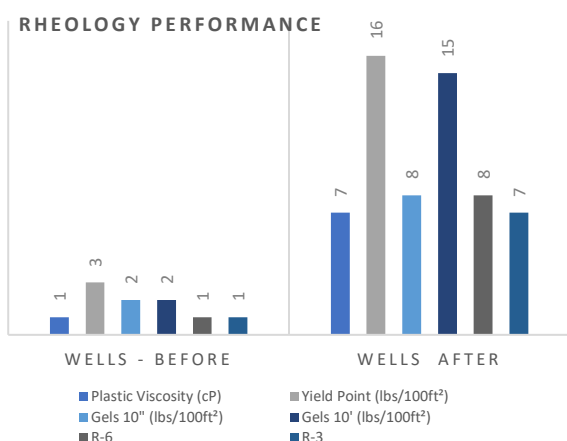


Figure 17. Graph of rheology performance in the well before and after using the novel uintaite water suspension

Table 6. Summary of results using the aqueous uintaite dispersion

Property	Result	Operational benefit
Quality of cuttings	No signs of splintering, clumps, or stickiness	Excellent wellbore integrity due to better shale control
Rate of penetration (ROP) improved	by 27%	Reduced cost
Torque reduced	by 21%	Increased efficiency lubricity
Casing run time was reduced	by 3.5 hours	Reduced cost
Avg. cost reduction	36 to 50%.	Only in the mud cost

**Conclusions**

- Nitrogen-based chemistry represents a leading edge in shale inhibition technologies for water-based mud (WBM) applications.
- The utilization of uintaite in WBM as a shale inhibitor has been extensively documented, showcasing its evolution

over decades as an effective means of shale inhibition across various mud systems and environmental conditions.

- The distinctive geochemistry of uintaite confers hydrophobic and hydrophilic properties, distinguishing it from other asphaltites and shale control materials and rendering it particularly effective when incorporated into water-based mud formulations.
- Geochemical analyses indicate that nitrogen content in uintaite is nearly 100% organic, predominantly present within pyrrole rings, making it readily available for chemical reaction.
- Further, geochemical investigations into uintaite elucidate the organic nitrogen's origin, confirming transformation from proteinaceous material into pyrrolic structures via diagenesis. The abundance of nitrogen in uintaite, as opposed to sulfur, is due to its type I kerogen classification defined by organic sediments deposited in freshwater environments in the Green River basin.
- The hydrophilic aspect of the innovative liquid uintaite suspension, comprising amine compounds and pyrroles, neutralizes negative charges within shale layers, while the hydrophobic aliphatic chains, facilitated by hydrogen bonds, repel water.
- Beyond activating functional groups for shale inhibition, the novel product enhances low shear rate viscosity (LSRV) and reduces the lubricity coefficient, reducing the need for supplementary mud additives.
- The novel uintaite-based product offers a dual-pronged approach to shale inhibition: chemically, through amphipathic interactions with polar and non-polar phases, and mechanically, by forming a slick and thin filter cake owing to its softening capabilities.
- Overall, the novel liquid uintaite suspension surpassed expectations in the Powder River basin field applications, signifying a paradigm shift in uintaite's utility in WBM as one of the most effective shale inhibitors, enabling full interaction of its organic nitrogen with shale layers.
- The application of uintaite suspension within KCl/polymer-based drilling fluid notably enhanced drilling, tripping, and casing-running operations during the construction of two wells (See Figure 17 and Table 6). These improvements resulted in significant time and cost savings for the operator in the Powder River Basin.

**Acknowledgments**

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**Nomenclature**

1. API = American Petroleum Institute
2. CP/MAS = Cross Polarization-Magic Angle Spinning

3. ESCA = electron spectroscopy for chemical applications (X-ray photoelectron spectroscopy or XPS)
4. ESI= Electrospray Ionization
5. FT= Fourier Transform
6. FT-ICR-MS = Fourier-transform ion cyclotron resonance mass spectrometry
7. GCMS = Gas Chromatography Mass Spectrometry
8. GPM =gallon per minute
9. HPHT =High Pressure High Temperature
10. LSRV= Low Share Rate Viscosity
11. NMR = Nuclear Magnetic Resonance
12. ROP = Rate of Penetration
13. TD =Total depth
14. WBM =Water Based Mud

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