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30 Years of Mixed-Metal Technology (MMH/MMO): Where Are We Now?

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Abstract

In 1987[1], the first patent was issued and the first field trial took place using mixed-metal hydroxide (MMH) in a drilling fluids application. Since then, these novel fluids have undergone significant improvements with respect to fluid performance and stability, most notably the introduction of mixed-metal oxide (MMO) chemistry.

These "mixed-metal" products are added to a water-based fluid along with clay, such as bentonite, attapulgite, or sepiolite, to produce a unique thixotropic, shear-thinning fluid that is highly viscous at low shear rates but becomes very thin at high shear rates and easily passes through fine screens. Early applications for the use of MMH fluids were targeted for use in unconsolidated formations and for milling operations due to the fluids unique flow profile and superior carrying capacity, respectively. However, in recent years more interest and usage of these fluids has been due to 1) the fluids innate ability to retain wellbore integrity, especially in high salt-containing and unconsolidated formations, and 2) the reduction of mud losses and lost circulation prevention in highly porous or fractured formations.

Here, we present a review of MMH/MMO technology over the last 30 years along with further developments in MMO technology, including higher temperature stability, better tolerance to anionic contamination, and especially a much higher endurance to increased calcium and magnesium salt concentrations than previous MMO technologies.

Introduction

Bentonite clay, specifically sodium bentonite, has been used when drilling for oil and gas for nearly a century. An ion exchange mechanism occurs when the clay is dispersed in fresh water that allows the clay to platelets align “edge-to-face” and in the process, progressively form a gel structure. When sheared, the gel structure is broken, and the fluid viscosity drops; when shear stops, the gel progressively re-forms, gradually increasing viscosity over time. This natural shear-thinning property of bentonite, when added to water, allows for the suspension of weighting agents, such as barite or hematite, and aids in the cleanout of the wellbore. Bentonite imparts resistance to oxidation and is durable when exposed to very high shear conditions, such as those present at a drill bit nozzle.

Clay-based rheological modifiers do suffer problems, as when in the presence of polyvalent cations, such as calcium or magnesium. These cations can lead to flocculation of the clay and undesirably high gel strengths, especially at higher temperatures, unless certain high-temperature mud thinners are in the system. The addition of too much clay can also cause excessive gel strengths which affects pumping pressures. Clays can also be combined with certain polymeric materials to improve deficiencies in the clay, however this can add complexity and/or cost.

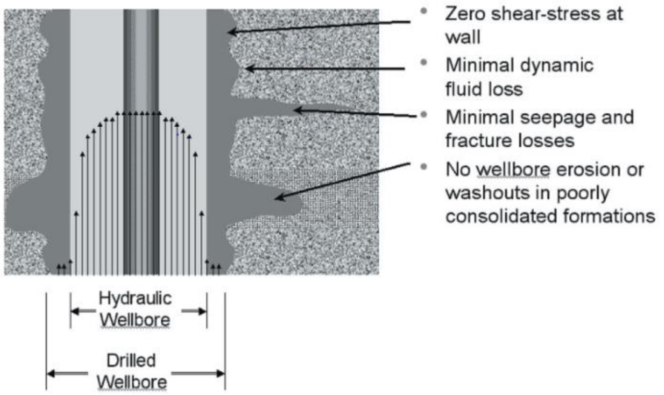


Figure 1. Schematic illustrating the annular velocity profile of a Mixed-Metal drilling fluid.[2]

For some applications, it is more desirable to have a viscous, highly thixotropic fluid that can be readily shear-thinned to a low-viscosity fluid when shear is applied, followed by a rapid and near-instantaneous reversion back to its original state when shear forces are removed. These properties are achieved when mixed-metal chemistry is incorporated into a bentonite drilling fluid.

These interesting properties can be exploited as a drilling fluid. As the liquid flows freely with low viscosity through the drill bit and up the annulus, the flow near the center of the wellbore continues as a typical fluid, however, the fluid nearest to the wellbore behaves more as a solid or pseudo-plastic (Figure 1) due to the limited amount of shear and flow velocity seen at the wellbore. This unique rheological property is derived from the interaction between the mixed-metal rheology modifier additive and bentonite in a water-based mud.

The nomenclature of the mixed-metal products has changed over the last few decades, and therefore can be confusing. The mixed-metal rheology modifiers have been described, formulated, and marketed under a variety of names over the past 30 years, with all providing similar rheological properties:

- MMLHC - Mixed-Metal Layered Hydroxide Compounds (Late 80's)
- MMH – Mixed-Metal Hydroxides (Mid-90's)
- MMOH – Mixed-Metal Oxy Hydroxides (Late 90's – Early '00's)
- MMO – Mixed-Metal Oxides (Mid-00's to present)

The early MMLHC and MMH compounds were expensive, very sensitive moisture and to contaminates in the drilling fluid, and required at least one pass through the drill bit to develop full viscosity. Significant improvements came when MMOH and MMO were developed, as these products were much more cost effective, much less sensitive to moisture (shelf life of months or years instead of days or weeks) and could develop viscosity quickly without requiring high shear. MMH also had the additive step of pre-mixing in a chemical barrel prior to incorporating into a mud system, whereas MMO could be added directly to the mud system in the same way bentonite was added. For simplicity, the authors will refer to these fluids in general as mixed-metal, or MM, fluids.

The mechanism of interaction with sodium bentonite was determined to be from the ion exchange mechanism where the positively charged sodium ions (Na^+) were replaced by the positive charges of the MM crystal. This complex is described as a "crystal salt". Due to this ionic interaction between the MM and the sodium bentonite, if other ions or group of ions entered the system that had a greater affinity to either the MM or the clay, the corresponding rheology resulting from the interaction between the MM and sodium bentonite would be lost. Large organic ions such as lignite, lignosulfonate, certain carboxymethyl celluloses/starches, and polyacrylates can significantly lower rheology, but smaller ions such as calcium, magnesium, chloride, carbonate, and sulfate do not cause significant rheological issues; however, if appreciable amounts of calcium and magnesium are a fluid, they can lower the overall rheology over time. Soda ash or potash are suggested additions to a fluid to remove hardness.

A simple mixed-metal fluid typically consists of the following additives added to water:

1. 6 to 12-lb/bbl pre-hydrated bentonite (attapulgite or sepiolite can also be used)
2. 0.6 to 1.2-lb/bbl mixed-metal additive
3. 0.25-lb/bbl soda ash
4. 2 to 6-lb/bbl of fluid loss additive, typically a non-derivatized or specially modified starch
5. Caustic Soda to keep pH between 11.0 – 11.5
6. Barite to desired weight

Clay Chemistry

Various clays can be used along with MM compounds. Sodium bentonite, hectorite, attapulgite, and sepiolite all interact in some way with MM compounds. Calcium-based clays, such as calcium bentonite, do not show appreciable rheology increases when added along with an MM compound. For best mud properties, a clay should be mixed in fresh water, sheared, and allowed to hydrate fully prior to the addition of the MM additive. Untreated high-purity bentonites provide the best rheology. Treated bentonites can be used, however treated bentonites typically contain small amounts of anionic polymer to boost viscosity performance of the clay, and these anionic polymers can counter the benefit of MM additive requiring additional MM to be added to the system.

The optimum clay to MM ratio needed is typically 10 parts clay to 1 part MM, although this could vary depending on the drilling situation.

Carbonates for Calcium Removal and pH

The use of sodium and potassium carbonate, soda ash and potash, respectively, in an MM system is highly recommended. The addition of soda ash removes calcium, which can reduce the viscosity of the system, but also has the secondary benefit of raising pH to around 10.5, which is close to the pH range the fluid needs to be in order to fully develop viscosity. Keeping calcium concentration below 400 mg/L is recommended.

Overtreatment of soda ash does not negatively affect rheology, as the excess carbonate does not interfere with the MM/bentonite complex. Potassium carbonate can be used as well, however is typically more expensive, but does provide additional potassium ions (K^+) for shale inhibition.

Caustic soda or caustic potash should be used to raise pH to above 10.5 (ideally 11.0 - 12.0).

Fluid Loss Additives

One of the caveats of the enhanced rheology of the MM fluid is that the bentonite loses its ability to form platelets on the wellbore and contribute to fluid-loss control, therefore a fluid loss additive is recommended to be used with the system. Since highly charged organic compounds can negatively affect rheology, white or yellow starch, which are non-ionic in nature, and/or special starch derivatives tailored for MM fluids should be used.

Anionic Suppressants

As mentioned previously, large organic ions can negatively affect system rheology, by preferentially binding to either the bentonite or the MM additive, or both. In prior years, if an MMLHC or MMH fluid was used in the field and the fluid encountered lignite or if somebody on site accidently added a sack of lignosulfonate, then the fluid viscosity would disappear, and a completely new batch of MMH mud would need to be built.

With the newer MMOH and MMO technologies, if anionic contamination occurs, a small amount of anionic suppressant can be added to the mud system to readily bring back viscosity. As a MM mud system builds up drill solids and becomes aged, it tends to acquire better stability characteristics over time and becomes more resistant to anionic contamination.

Overview of MM

The following subsections discuss MM technology over the last 30 years; how it was used, why was it used, and the related field case studies that display the benefits of the system.

Burba, Barnes (1987) – A New Technology[1]

In the late 1980's, the Dow Chemical Company developed a new, interesting crystal compound that consisted of a mixture of lithium, aluminum, and magnesium hydroxides and had a very high cationic charge density on the surface of the crystal. They found that when this highly cationic crystal interacted with the anionic surface of a clay, such as sodium bentonite, at pH 10 or above, the corresponding electrostatic interaction produced very high gels with desirable pseudoplasticity at various shear rates – very thin, water-like fluid at high shear rates and very thick, high-yield-point properties at low shear rates. Other products such as aluminum hydroxide ($Al(OH)_3$), produced a somewhat similar gel with bentonite, however the rheology varied depending on whether certain carbonate salts were present and required pH below 7 to remain stable, which isn't a pH range typically desired for a water-based mud.

These mixed-metal hydroxide, MMH, crystals were shown to be extremely thin, between 8 to 16 angstroms in thickness and consisted of only a single monolayer that was hundreds of nanometers in length. Due to the reactivity of the MMH crystals, and when they were produced, a polyol such as glycerin or polyglycerol, was added to the product prior to drying to stabilize the crystals. Because of this stabilization treatment, using MMH in a field operation required the use of a chemical barrel to pre-mix the MMH in water prior to the incorporation into the mud pit.

The authors found that when the MMH was added to as little as 0.5% by weight sodium bentonite in water, the viscosity significantly increased, along with a large increase in yield point (YP) and only a very slight increase in plastic viscosity (PV). They also found that the bentonite/MMH suspension was thermally stable to around 400°F, even though bentonite can thermally flocculate around 300°F if not dispersed.

Burba, Holman, Crabb (1988) – Shale Inhibition and Early Field Evaluations[3]

The authors demonstrated the use of mixed-metal layered hydroxide compounds (MMLHC's) as a water-based drilling fluid additive that provides an unusual type of shale inhibition, solids suspension, and resistance to contamination along with field test data.

The suspension characteristics of the fluid were described as remarkable. When 5 lb/bbl of sodium bentonite was added to 0.7 lb/bbl of MMLHC, the fluid had a yield point of 26 lb/100 ft^2 and a plastic viscosity of 4 cP. When gravel screened to 8 mesh in size was added to the fluid, the gravel stayed suspended for over 2 years. However, when the container was tilted, the fluid easily flowed.

Shale inhibition was evaluated in several ways, such as the addition of calcium montmorillonite, Pierre shale, and South Louisiana gumbo shale in two different fluids as clay contaminates. The two fluids were an MMLHC fluid that consisted of 10 lb/bbl of sodium bentonite and 1.0 lb/bbl of MMLHC, and a dispersed bentonite fluid consisting of 20-lb/bbl bentonite and 6-lb/bbl chrome lignosulfonate with sodium hydroxide added to reach pH of 9.5. In each case as more contaminates were added to the fluids, it resulted in off-scale viscosity increase and high yield point for the dispersed fluid while the MMLHC fluid initially decreased or had little to no increase in viscosity, then gradually increased over time while handling significantly more drill solids than the dispersed bentonite fluid. The authors noted that the initial decrease in the MMLHC fluid viscosity when the clay contaminates were added was attributed to the excess MMLHC's in the fluid interacting with the contaminates.

Shale erosion testing was also performed with Pierre shale, where increasing amounts of MMLHC's were added to a bentonite system in seawater, from 0 to 1.5 lb/bbl, and was aged at 150°F for 16 hours, as shown in Figure 2. Additional MMLHC added to the bentonite fluid resulted in a significant increase in the percent of shale recovered, from 20% recovery for a bentonite fluid to over 80% recovery when 1.5-lb/bbl MMLHC was added. The addition of potassium chloride (KCl) at 6% concentration to the MMLHC system was also shown to be additively beneficial. The authors also noted that the while an increase in pH typically leads to increasing shale dispersion in conventional systems, they received the greatest shale recovery for MMLHC fluids when the pH was greater than 9.

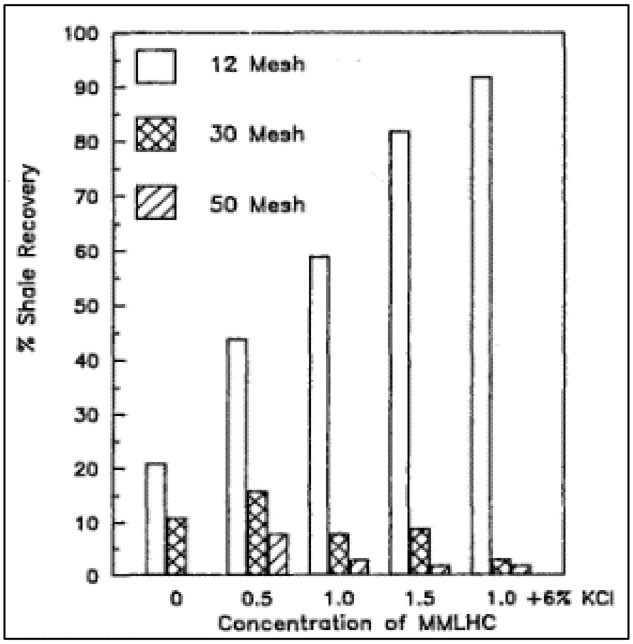


Figure 2. Bar graph and % recovery of Pierre shale vs. concentration of MMLHC in a seawater fluid after 150°F hot roll for 16 hours.[3]

Two field evaluations were constructed using the MMLHC chemistry, both of which took place in North Central Texas, referred to as Albright #1 and Mead #1. The troublesome area in this region is the Midway shale from 1,900 ft to 2,850 ft. At the time, the best practices in the region were to drill through the Midway section as quickly as possible before the formation begins to slough and soften.

For the Albright #1 well, at 1,600 ft the mud was converted to MMLHC and was further treated with 1.5 lb of MMLHC for each barrel of water added to the system. No sloughing or hole problems were encountered and the shale cuttings obtained were firm and distinct, indicating inhibition. The cuttings discharge rate remained consistent, suggesting that the solids remained suspended during bit trips. The larger pieces of shale recovered, determined to be between 40-45% smectite clay, did not disperse when placed in water. When the recovered shale was allowed to dry out and crack and placed in water, it immediately dispersed. The authors suggested that the bentonite-MMLHC complex formed a film on the surface of the cuttings, inhibiting dispersion.

The Mead #1 well was an offset well drilled within 2,500 ft of the Albright #1 well. The difference between the wells was that the Mead #1 well was drilled entirely with the MMLHC fluid. The well was uneventful, the hole remained very clean, and logging tools had no problem getting to the bottom of the hole. Both the Mead #1 and Albright #1 wells were compared to an offset well drilled with a conventional fluid. In both cases, the two wells drilled with the MMLHC fluid drilled 15 to 20% faster than the conventional fluid system.

Polnaszek, Fraser (1991) – Better Understanding of MMH and use in Offshore Gulf of Mexico[4]

During this period, the product chemistry was referred to more simply as Mixed-Metal Hydroxide (MMH) and Polnaszek and Fraser developed a better understanding of why the MMH complex created the unique rheological properties described prior. Further understanding of the properties during this time led to MMH fluids being developed as an independent mud system, instead of as a minor additive component to a conventional fluid.

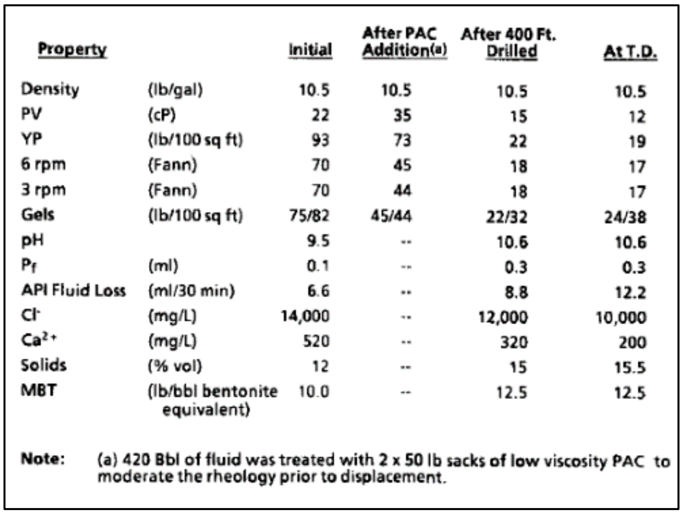
The MMH's are electron deficient, leading to the high positive charge density on the MMH surface, making it dispersible but not soluble in water. The authors determined that the charge density of the clay/MMH complex is 6 to 7 times higher than the clay itself. This high charge density results in a much higher electrostatic field that enhances the organization of associated water surrounding the complex, leading to electrostatic influence that extends far past the typical charge boundary of a typical clay platelet. It is believed that the clay and MMH do not have very much physical contact due to the "water of hydration" associated with the complex; when the fluid is at rest, the structure is highly organized, where sheets of complexes and bound water occupy the spaces between the sheets.

The rheology properties of the fluid are described as more of an elastic solid or pseudo solid than that of a conventional liquid, even though a simple MMH/bentonite slurry consists of approximately 97% water. The fluids have a significant capacity to suspend large solids, but requires much less energy to break the gels that are formed, when compared to other typical fluids. If the same suspension capacity is present in conventional bentonite or biopolymer fluids, then potential pumping or surge/swab pressure issues could arise.

Progressive gel strengths are near nonexistent as very fast gel formation correlates to similar measurement readings at low shear rates. Unweighted MMH slurries, in their simplest form, typically give the 6 RPM, 3 RPM, 10 sec gel, 10 min gel, and 30 min gel readings in a narrow range, however it is not uncommon for them to be identical.

An opportunity arose to use an MMH fluid in a shallow offshore horizontal well in the East Cameron parish area offshore Louisiana. The area was a shallow gas sand play with high permeability. The operator needed a fluid that ensured superior hole cleaning when drilling and could suspend sand, cuttings, and weighting material when circulation ceased, but also should be easy to reinitiate circulation once pumping resumes. A conventional fluid with high gel strengths may be suitable for suspension, however if used in a horizontal section may require excessive pump pressures to resume circulation. Another desirable characteristic of the fluid is that it shouldn't wash out poorly consolidated sands, as an out-of-gauge hole could be detrimental to completing the well. All the concerns of the operator were addressed by using an MMH/bentonite fluid system weighted up to 10.5 lb/gal using calcium carbonate or salt, with the use of a modified polysaccharide to assist with fluid loss control.

Table 1. MMH Fluid – Field Properties of East Cameron Block 265 B-12 Well.[4]



Property		Initial	After PAC Addition(a)	After 400 Ft. Drilled	At T.D.
Density	(lb/gal)	10.5	10.5	10.5	10.5
PV	(cP)	22	35	15	12
YP	(lb/100 sq ft)	93	73	22	19
6 rpm	(Fann)	70	45	18	17
3 rpm	(Fann)	70	44	18	17
Gels	(lb/100 sq ft)	75/82	45/44	22/32	24/38
pH		9.5	--	10.6	10.6
P_f	(ml)	0.1	--	0.3	0.3
API Fluid Loss	(ml/30 min)	6.6	--	8.8	12.2
Cl^-	(mg/L)	14,000	--	12,000	10,000
Ca^{2+}	(mg/L)	520	--	320	200
Solids	(% vol)	12	--	15	15.5
MBT	(lb/bbl bentonite equivalent)	10.0	--	12.5	12.5

Note: (a) 420 Bbl of fluid was treated with 2 x 50 lb sacks of low viscosity PAC to moderate the rheology prior to displacement.

When the system was evaluated using a high-temperature, high-pressure rheometer at a constant pressure of 2500 lb/in^2, but increasing temperature, from 77°F to 190°F, an interesting trend was noted. As temperature increased, the low shear rate also increased, where the reverse trend is typical of clay-free polymer fluids.

The authors also noted that when motion is added, the pseudo-solid structure "snaps" and a localized change of physical state occurs. This was observed in a field setting when rice grains were used to determine bottoms up time on an 11,000-foot directional offshore well. The rice returned to the surface much earlier than expected, based on hole gauge, indicating the possibly of channeling occurring. Assuming a gauge hole, they determined that only 75% of the fluid volume was moving. They calculated that if the drill pipe was positioned in the center of the hole and the static layer of mud was distributed evenly farthest from the area of mechanical action (the rotating drill pipe), then there would be a ¾-inch-thick "stationary" layer on the wellbore.

For the offshore well, they formulated a mud using a 10-lb/bbl equivalent of a Wyoming bentonite slurry that was pre-hydrated in fresh water and added to seawater. The fluid was treated with 0.5-lb/bbl soda ash to treat out hardness. Afterwards, 1 lb/bbl of MMH was "pre-wetted" in a chemical barrel and added to the fluid to develop viscosity, along with 4.75 lb/bbl of modified polysaccharide and enough calcium carbonate to weight up the fluid to 10.5 lb/gal.

The MMH fluid was displaced into the hole without any issues. The pumping equipment and mud hoppers were not impaired by the system. Despite the viscous nature of the initial fluid, shown in Table 1, there were no issues with the fluid flowing through the shaker screens ranging from 50 mesh to 100 mesh.

Also noted was the appearance of the MMH fluid in the mud pit. It does not have the appearance of a typical mud, as it does not look like a dispersed or polymer mud system. Due to the high low-shear-rate rheology, the fluid gels up when there is no agitation in the surface mud pit, but when the pumps or rotary mixers are on, the MMH fluid flows freely. It may appear that the fluid has deteriorated, but once agitation ceases, the gels reform. This unfamiliar appearance of the MMH fluid should be expected, as it is a consequence of the superior and unique rheological properties of the fluid.

Throughout drilling, the hole appeared to be in gauge with no associated tightness from the hole. The well had high initial and sustained production rates, which was evidence to support the minimal danger associated with a calcium carbonate/MMH system in a production zone. When the fluid was displaced by calcium chloride completion brine, the MMH/clay complex dropped viscosity. There were also no issues with downhole measurement/logging equipment. The drill bit performed fine, as the hole was always clean and open. A second shallow gas well was drilled onshore nearby using an MMH fluid with similar good performance.

Fraser, Reid, Williamson, Enriquez (1995) – Insight on MMH Fluids Used in Production Zones[5]

The authors focused on 3 primary objectives when evaluating MMH fluids in an oil or gas producing formation. They wanted to:

1. Investigate the mechanism of filtercakes on sandstone.
2. Study the nature of the cakes of different drill-in fluids.
3. Investigate filtercake cleanup.

MMH fluids are unique in its ability to form a predominately external filtercake when deposited on a wellbore. This is due to the strong interactions between MMH and the complexed bentonite, which prevents the formation of a damaging internal filtercake. The external filtercake formed by an MMH fluid is removed easily by wash fluids by application of back pressure when the well is brought onto production. The rapid formation of a strong, low-permeability cake is central to minimizing fines invasion, which is why it's common to add bridging materials to aid in fast cake development. A fluid needs to protect cake formation, but the filtercake should be easily removed.

There are two common methods embraced for filtercake removal – remove the filter cake using breakers or force the cake to lift off during well flow. Here, the authors focused on cake lift off as a better method under the premise of "prevention is better than the cure".

One of the evaluations relied on scanning electron microscope (SEM) imaging to determine fluid invasion within Clashach sandstone. Comparison was between two primary fluids: a Polymer/KCl fluid and a Bentonite/MMH/Carbonate fluid.

The results reaffirmed that bridging materials can be effective at minimizing early time fluid intrusion, which is believed to be responsible for the majority of formation damage from the intrusion of fines into the formation. When evaluating a Polymer/KCl fluid, no external cake was formed as 200 microns of internal filter cake invasion was present (Figure 3). When the Bentonite/MMH/Carbonate fluid was evaluated, it left an entirely external cake (Figure 4). The rapid and strong attraction of MMH and bentonite platelets is also responsible for early time bridge formation and minimization of fines invasion. Fines invasion was also seen when testing a conventional weighted bentonite/carboxymethyl cellulose (CMC) fluid, validating the perception of conventional bentonite-based fluids having the potential for damaging oil and gas producing formations.

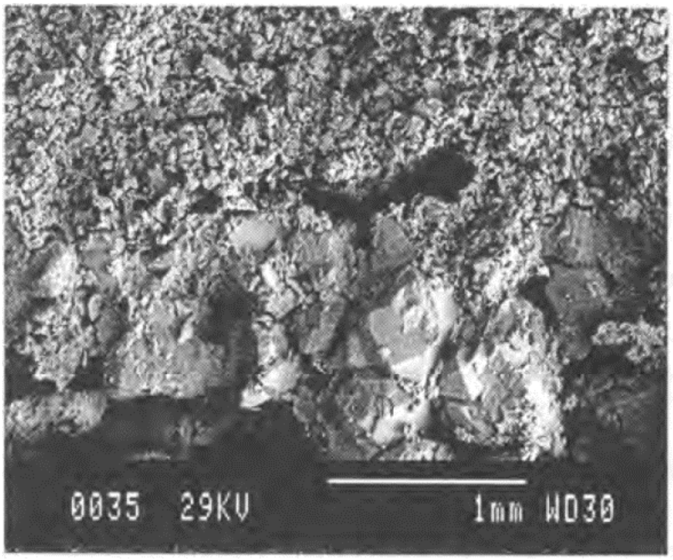


Figure 3. Invasion of solids during deposition of polymer/salt cake on Clashach sandstone.[5]

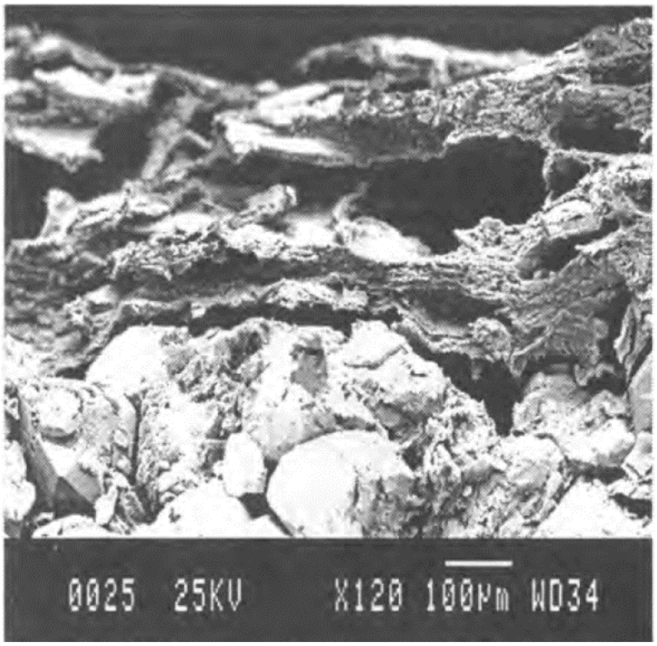


Figure 4. Closeup of unweighted MMH fluid/ Clashach sandstone interface showing extended cake.[5]

Return permeability studies were also performed using 3 different fluids:

1. Polymer and Carbonate fluid
2. Polymer and Salt fluid
3. MMH and Carbonate fluid

The fluids were evaluated on core samples of Clashach and Birchover sandstones that were saturated with NaCl/CaCl$_2$ brine before applying 10 lb/in^2 of pressure to flow kerosene through the core until a steady flow rate was achieved. The core was then exposed to the test fluid for 60 minutes in either static condition or at a 300-lb/in^2 differential in pressure. After the outer cakes were removed, the cores were back flushed with kerosene at 10 lb/in^2 and the recovered permeability was determined as a percentage of the initial flow.

Using Birchover sandstone, all fluids indicated 100% recovery, primarily due to the smaller pore size of the Birchover sandstone, relative to the Clashach sandstone. As for the Clashach sandstone, all fluids under static conditions provided the same percent recovery within experimental error (85 – 90% recovery).

In addition to the return permeability studies, the authors performed a cake liftoff study using the same three fluids mentioned in the return permeability experiment. Similarly, the core was prepared as before using 10 lb/in^2 of pressure, but filter cakes were grown for 240 minutes under a pressure of 300 lb/in^2. Afterwards, the filter cakes were left in place and were back flushed with 10 lb/in^2 of kerosene and a percent flow recovery was determined. Initial permeabilities were established at 2 lb/in^2 and slowly ramped up to 10 lb/in^2, where at different intervals of pressure, the percentage permeability recovery was measured.

The lowest permeability recovery was from the Polymer/Salt fluid, and of the flow that made it through, it appeared to come from pinholes within the filter cake. The Polymer/Carbonate and MMH/Carbonate filtercakes performed much better and were of similar performance; however, the mechanisms were different. The Polymer/Carbonate cake ruptured and tore, allowing flow through punctured holes. As for the MMH/Carbonate fluid, the entire cake lifted off the core. Even at low back pressures, the MMH/Carbonate filtercake began to separate from the core and eventually separated completely.

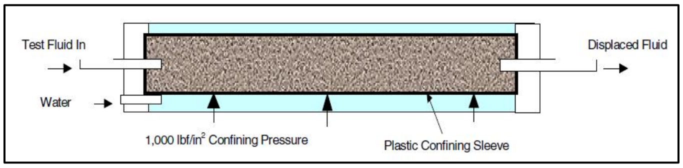


Figure 5. Apparatus used to investigate fluid flow through wet sand pack.[5]

Field mud studies were also performed with both MMH/Carbonate and Polymer/Salt fluids. Both fluids had return permeabilities of 70-75%, however the addition of more MMH to the MMH/Carbonate system resulted in complete permeability recovery. Static filtration data for the unaltered field MMH fluid filtered at 200 lb/in^2 on Ketton limestone appeared to develop an internal cake, which would be typical of a conventional bentonite fluid. The addition of 1 lb/bbl of MMH to the field mud reduced the early spurt loss, and very little spurt volume was obtained when 2 lb/bbl was added. As additional MMH was added to the system, the cake changed from an internal cake to an external cake. The authors also state that there is a strong indication of the unique rheology properties of the MMH system and the formation of bridges that limits the movement of fine solids into the rock. The mechanism appears to be between the interaction of clay platelets and MMH crystals.

Fraser, Aragão (2001) – MMOH Fluid Used in Ultra Deepwater Situation with Narrow Pressure Window[6]

A Mixed Metal Oxy Hydroxide (MMOH)-based fluid, a more stable version of the original MMH technology, was used in an ultra-deepwater application off the coast of Brazil. For the sake of consistency, the authors referred to the slightly different chemistry of the MMOH as simply “MMH” as the system was more commonly known.

Due to the narrow pressure window, the equivalent circulating density (ECD) values exceeded the measured leak-off pressure at the casing shoe by 0.5 lb/gal, however no losses were recorded, and the well was drilled to total depth (TD). An MMH fluid was chosen due to several reasons:

- Unconsolidated formations are less likely to be a problem with an MMH fluid due to static mud layer on the wellbore.
- In the likely event of increasing ECD causing formation fractures, as the fluid travels to the furthest point away from the influence of the rotating pipe, the fluid will likely be in a solid state.

MMH fluids have been used with varying degrees of success, and while not always successful, there was significant improvement observed in most cases. Losses due to porous and fractured formations, as well as wellbore washout, were all reduced. The best way to minimize losses while drilling naturally fractured formations is to have as little erosion on the wall as possible by reducing the shear rate at the wall.

To demonstrate the rapid increase in viscosity of the MMH fluid at low shear rates, a lab-prepared wet-sand pack was used to evaluate the flow of high-viscosity polymer fluids, bentonite fluids, and MMH-based fluids (Figure 5). The sleeve was packed with 40/100 mesh sand and confined using 1,000 lb/in^2 to eliminate channeling inside the sleeve. Fluid was pumped at a rate of 50 mL/min using a syringe pump and the pump pressure was monitored and set to shut down if the pressure exceeded 250 lb/in^2.

When pumping water through the sand-packed sleeve, a pressure of 2-4 lb/in^2 was obtained. When evaluating high-viscosity bentonite and biopolymer slurries, the pressure rose to 160 lb/in^2 and 140 lb/in^2, respectively as the slurries traveled through the sleeve. When the MMH fluid was pumped through the sleeve, the fluid only reached around 2 inches in when the pressure rose rapidly to exceed 250 lb/in^2 causing the pump to shut down.

For the deepwater field mud, the leak-off weight was 9.2 lb/gal but the maximum ECD of the fluid was 9.7 lb/gal, or 0.5 lb/gal above measured leak off. Normally losses would be expected but were absent using the MMH fluid. At times where bit balling appeared to be occurring, the incorporation of KCl was included in the system. While the KCl aided in inhibition, it's effects were negligible on the rheology of the system, however it did lower fluid-loss performance. As more active drill solids were added to the mud, these were treated using 1-lb/bbl MMH, 3-lb/bbl fluid-loss additive, and 15-lb/bbl KCl.

Another unusual characteristic of the MMH slurries is the change in rheology with variation in temperature. As most fluids show a reduction in low-shear-rate viscosity with increasing temperature, MMH fluids behave in the opposite manner, as shown by high-temperature, high-pressure rheology measurements, as shown in Figure 6. In the laboratory prepared mud evaluation, as the temperature increased, the PV decreased and YP and low shear viscosity increased.

When the field mud was evaluated under similar conditions, the YP and low-shear-rate viscosity also dropped with increasing temperature. The authors assumed that since conventional drilling fluid additives were in the system, such as the polymeric fluid-loss-control additives, that they added a conflicting "conventional" mud property to the fluid that ended up being a balance between the MMH properties and the "conventional" mud component properties.

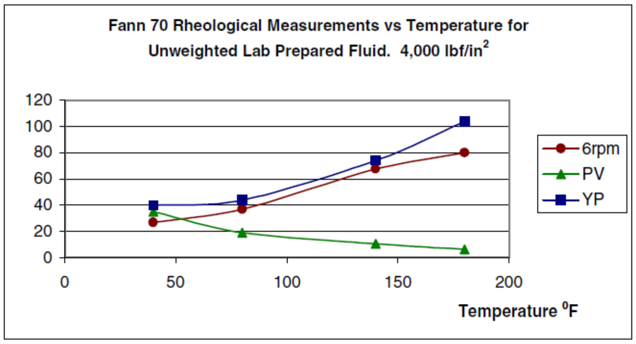


Figure 6. Rheological data for lab prepared fluid generated with Fann 70 showing various parameters with variation in temperature at 4,000 lb/in^2 fixed applied pressure.[6]

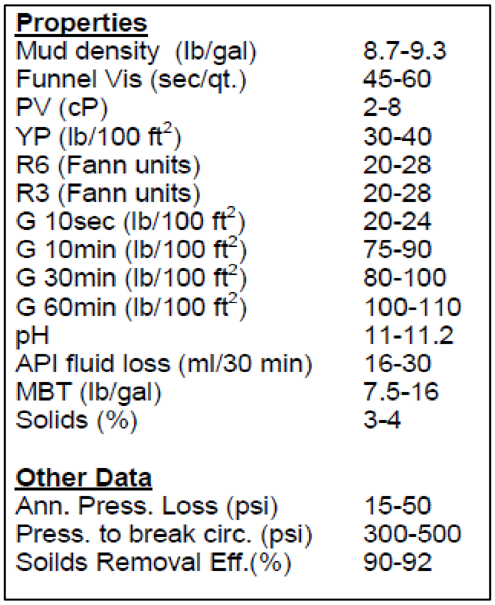
Fraser, Harrington, Albarrazin, Snyder, Donham (2003) – Usage and Case History of MMO Fluid to Prevent Mud Losses[7]

In the early 1990's, there was evidence that the rheological properties of an MMH fluid may impede the flow into fractures and porous media. Modeling showed that an MMH fluid should lose less volume along a fracture before a steady state was reached, when compared to other fluids typically used in similar types of formations. Laboratory work confirmed this theory when both conventional and MMH fluids were passed through a water-wet frac-sand column with a pressure shut-off limit; the conventional fluids passed through the column within the pressure limit, while the MMH fluid traveled only partly through the column before the pressure shut-off limit was reached.

The authors used a mixed metal oxide (MMO) fluid in their field trials in Argentina and Louisiana. The MMO had been developed and marketed as a more stable alternative to the MMH and MMOH products previously used.

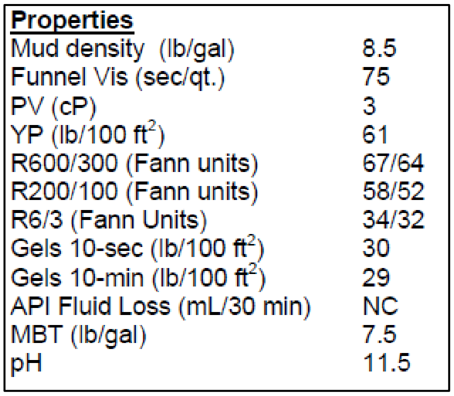
Their first case history was in Tartagal, Salta, Argentina. The fluid was used in the 28-in. section of the well, in an area notorious for very high whole fluid losses. Fluid properties are shown in Table 2. The section was drilled with a 40% reduction in mud losses (around 5,000 bbl vs. over 8,800 bbl for average offset wells). Also noted was the fluid's property to thin during solids removal, which allowed for the use of very fine screens on scalpers and linear shakers.

Table 2. Fluid Properties and Drilling Data from Argentinian Well.[7]



Properties	
Mud density (lb/gal)	8.7-9.3
Funnel Vis (sec/qt.)	45-60
PV (cP)	2-8
YP (lb/100 ft^2)	30-40
R6 (Fann units)	20-28
R3 (Fann units)	20-28
G 10sec (lb/100 ft^2)	20-24
G 10min (lb/100 ft^2)	75-90
G 30min (lb/100 ft^2)	80-100
G 60min (lb/100 ft^2)	100-110
pH	11-11.2
API fluid loss (ml/30 min)	16-30
MBT (lb/gal)	7.5-16
Solids (%)	3-4
Other Data	
Ann. Press. Loss (psi)	15-50
Press. to break circ. (psi)	300-500
Soilds Removal Eff.(%)	90-92

Table 3. Initial Fluid Properties from Louisiana Well.[7]



Properties	
Mud density (lb/gal)	8.5
Funnel Vis (sec/qt.)	75
PV (cP)	3
YP (lb/100 ft^2)	61
R600/300 (Fann units)	67/64
R200/100 (Fann units)	58/52
R6/3 (Fann Units)	34/32
Gels 10-sec (lb/100 ft^2)	30
Gels 10-min (lb/100 ft^2)	29
API Fluid Loss (mL/30 min)	NC
MBT (lb/gal)	7.5
pH	11.5

After the 28-in. section was drilled, they continued to use the fluid for a highly variable 22-in. section based on fluid performance due to improvements in ROP, wellbore stability, and control of whole mud losses. In the 22-in. section, over 3,000 bbl of MMO fluid was lost, compared to almost 9,000 bbl of mud lost in two other offset wells. LCM pills were also mixed when losses were encountered in the MMO system, however in some cases the losses were controlled before the LCM pill ever left the surface.

In the second case history drilled in Southeast Gueydan Field, Vermillion Parish, Louisiana, an MMO fluid was selected to drill a 20-in. section with the hopes of alleviating losses to avoid lost time. Mud properties are shown in Table 3. The system rheology was originally lost when they encountered lignite while drilling, which was anticipated, and a secondary fluid was prepared. There were partial losses through massive sand sections encountered at 1,000 to 2,600 ft. Wells drilled in this area typically had very high losses due to old oyster beds below 5,000 to 5,800 ft; however in this 20-in. section using the MMO fluid, the well was drilled without complete losses of returns for the very first time and they did not see pea gravel or collapsed oyster beds that they've seen in nearby wells.

Oswald, Marinescu, Vlasceanu (2007) – MMO used to Cure Lost-Circulation Issues while Meeting Environmental Regulations[8]

By 2007, the original MMH chemistry was no longer used due to its high production costs and short shelf life. The primary chemistry used its place was MMO, or a variant thereof. There continued to be interest placed in not only the fluid's unique rheological properties, but also the beneficial property of the system being environmentally benign. When drilling in an area with strict environmental regulations, such as REACH regulations in the European Union, emphasis on mud waste and disposal are increasingly important.

There were various applications in which MMO was used: unconsolidated formations, horizontal drilling, lost circulation, and even in the payzone. Most previous applications for MMO were for its use in lost-circulation control. The rheology of the system reduces losses from seepage in very porous or unconsolidated formations, to complete losses in fractured formations.

The authors show data, between years 2006 – 2007, from 11 wells with a high probability of losses, where 9 wells were drilled with an MMO system and 2 offset wells drilled with conventional water-based polymer fluids.

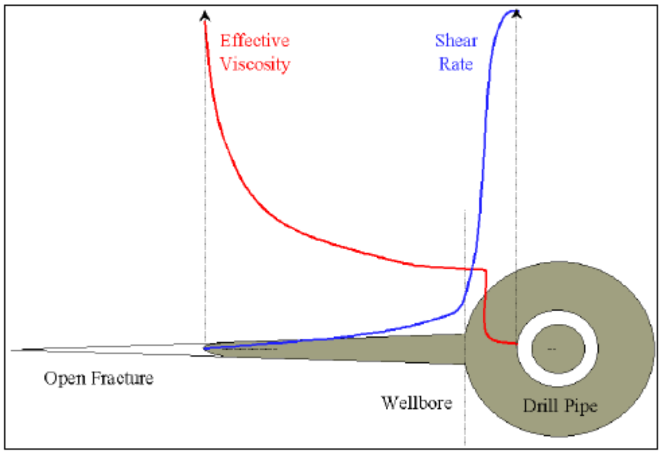


Figure 7. MMO Fluid Flow into a Fracture.[8]

The ability of an MMO fluid to reduce losses arises from the increase in viscosity of the fluid as it travels farther away from a source of shear, shown in Figure 7. Drilling fluid flows into an existing fracture if there is hydrostatic pressure exceeding formation pressure. The shear rates are high and therefore fluid viscosity will be low and whole fluid invasion will occur. The more volume that flows into the fracture, the greater the pressure required to keep and maintain flow into the fracture. Since hydrostatic pressure is constant, the flow rate declines and the viscosity of the fluid in the fracture increases. As the viscosity increases, the rate at which mud is lost decreases until it reaches a steady state and losses to the fractures stop. The same mechanism takes place in porous formations.

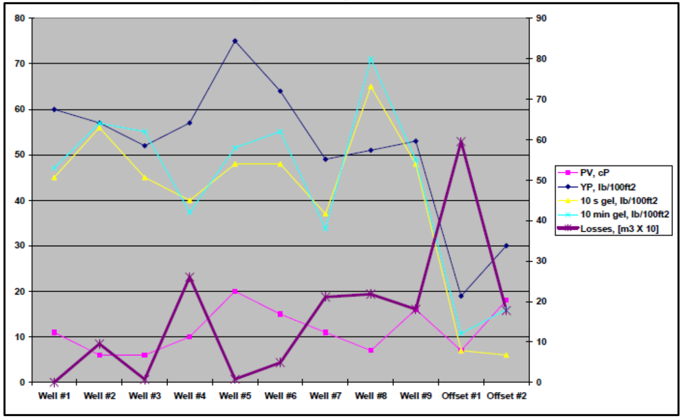


Figure 8. Rheology of MMO and Polymer System with Corresponding Mud Losses.[8]

Of the 9 wells drilled with an MMO-based fluid, there were almost no losses in 3 wells, 2 wells had moderate losses, and the remaining 4 wells had losses relatively higher, however the time to cure the losses was less than that of the offset wells (2 days for MMO-based fluid vs. 12.5 days for the offset wells).

The authors also noted that there appeared to be a rough correlation between the rheology of the fluids and the resulting volume of mud lost, where a higher rheology was shown to provide reduced mud losses (Figure 8).

Not only did the MMO fluids reduce the total mud volume lost in an area where mud losses are a common problem, but it also provided a better environmentally friendly alternative fluid system in a region where waste and disposal considerations are inherently necessary.

New Developments

Over the last several years, new developments in MMO chemistry have taken place to improve the effectiveness and robustness of the fluid system, while keeping the unique rheological properties associated with an MMO system. Some of the issues include the need for better rheological stability at temperatures greater than 300°F, better rheological performance in high hardness environments, better shale inhibition properties, and better tolerance to contamination from large ionic organic compounds.

High-Temperature Stability

Early MMH products had very high-temperature stability when complexed with bentonite (up to at least 400°F).[2] With the introduction of MMO chemistry, stable to around 300°F, this higher temperature stability property was lost at the expense of better performance, shelf life, and handling of the product.

A new higher temperature version of MMO, referred to as HT-MMO, has been introduced recently that allows for increased stability, especially at temperatures approaching 400°F compared to previously available grades of MMO. A typical MMO fluid would degrade at temperatures above 300°F and reduce viscosity to that of low-concentration bentonite fluid.

To show the enhanced viscosity of the product at elevated temperatures, laboratory rheological evaluations were performed on a simple HT-MMO system at various mud weights, from 10 to 16.0 lb/gal, after the samples were hot rolled at 350°F. The samples were prepared by adding 8 lb/bbl of a pre-hydrated premium-grade untreated bentonite, 0.8 lb/bbl of HT-MMO, 0.25 of lb/bbl soda ash, enough barite to weight up fluid to appropriate weight, and enough caustic soda to raise pH to above 11.0. The results were evaluated using a Fann 35 rheometer and are shown in Table 4.

All the results show extremely flat rheology. The highest mud weight evaluated showed very high viscosity; so high that it was almost off scale. To thin the mud back to a more reasonable rheology, an anionic suppressant (AS) was added to a newly prepared sample at 1 lb/bbl and hot rolled in the same manner as previous samples. The AS acts as a thinner/dispersant for high solids-laden fluids, along with its primary role of removing anionic contamination to restore rheology.

As temperature increases beyond 300°F, starches and modified starches will typically degrade quickly and become inefficient to use as fluid-loss additives. Special high-temperature polymeric additives can be added to a system with HT-MMO to provide fluid-loss control without significantly affecting system rheology or performance at high temperatures.

Table 4. Rheology of HT-MMO Fluids After Hot Roll at 350°F with Increasing Mud Weight.

Rheology @120°F	10.0 lb/gal	12.0 lb/gal	14.0 lb/gal	16.0 lb/gal	16.0 lb/gal + AS
600-rpm Reading	46	95	186	298	105
300-rpm Reading	42	91	183	297	99
6-rpm Reading	28	65	170	226	93
3-rpm Reading	27	64	166	197	92
PV (cP)	4	4	3	1	6
YP (lb/100 ft^2)	38	87	180	296	93
10-sec Gel (lb/100 ft^2)	21	52	109	173	32
10-min Gel (lb/100 ft^2)	48	56	122	297	46
pH	11.28	11.07	11.01	11.28	11.11

Compatibility in High Hardness Environments

Large concentrations of divalent ions like, calcium (Ca^{+2}) and magnesium (Mg^{+2}), have traditionally wreaked havoc on bentonite-based and polymer-based systems. These ions are typically introduced into a mud system via salt formations, produced brines, or seawater and are typically treated out using soda ash to keep mud properties consistent.

For these high hardness systems, a divalent ion tolerant MMO product has been developed, referred to as DV-MMO, to withstand and tolerate excessive amounts of divalent ions with temperature stability up to 250°F. While pH is important for MMO products, it can be challenging to increase pH of a high-concentration salt brine. Lime can also be used to raise pH along with caustic soda due to the calcium tolerance of the system.

To evaluate performance, three muds were prepared: an unweighted base mud with no DV-MMO, an unweighted mud that included DV-MMO, and a weighted mud that included DV-MMO. A high hardness brine was prepared by adding dry calcium chloride pellets to seawater to produce a fluid containing a calculated 48,400-mg/L calcium and 103,000-mg/L chlorides. To this brine, 10-lb/bbl pre-hydrated premium-grade untreated bentonite was added, then DV-MMO, and barite as required. A total of 8 lb/bbl of lime was added to each mud to raise pH. Results are shown in Table 5.

The rheological profile, while not as high as a typical MMO fluid, still retains the rheological characteristics of an MMO fluid, such as low PV, high YP, flat rheological profile, and flat gels. For increasing rheology of the DV-MMO system in high hardness conditions, several steps can be taken:

- The addition of soda ash to remove calcium and can boost performance
- Increase mud weight
- Increase concentration of bentonite/DV-MMO

Table 5. Rheology of DV-MMO Fluids After Hot Roll at 250°F.

Rheology at 120°F	No DV-MMO	DV-MMO unweighted mud	DV-MMO weighted mud
Mud Weight (lb/gal)	9.76	9.76	12.0
600-rpm Reading	9	41	46
300-rpm Reading	6	37	37
6-rpm Reading	3	19	20
3-rpm Reading	3	19	19
PV (cP)	3	4	9
YP (lb/100 ft^2)	3	33	28
10-sec Gel (lb/100 ft^2)	3	17	16
10-min Gel (lb/100 ft^2)	7	17	17
Initial pH	6.82	6.62	6.85
pH Adjusted	7.31	7.38	7.20

Shale Inhibition and Stability

Shale inhibition in MM fluids has been troublesome over time due to many types of shale inhibitors being large, complex organic ions (sulfonated asphalts, polyamines, PHPA's, etc.) and their interference with the bentonite-MM interaction. Various potassium salts do provide shale inhibition in MM fluids, however, at high concentrations they can lower rheology of the fluid, which is true for most salt brines in MM fluids.

Burba et al.,[3] showed that increasing the amount of MM additive to a fluid, beyond what is needed to complex with bentonite, can reduce the amount of shale erosion that takes place via mechanical surface effects. The addition of KCl aided in the inhibition.

Further research into shale inhibition additives for MM systems has resulted in the development of a new polymeric additive that can be added directly to a mud system in relatively small quantities and does not negatively interfere with system rheology, referred to as MMO-SS for "shale stability". It also has a very beneficial added effect of significantly increasing the system's tolerance to anionic contamination.

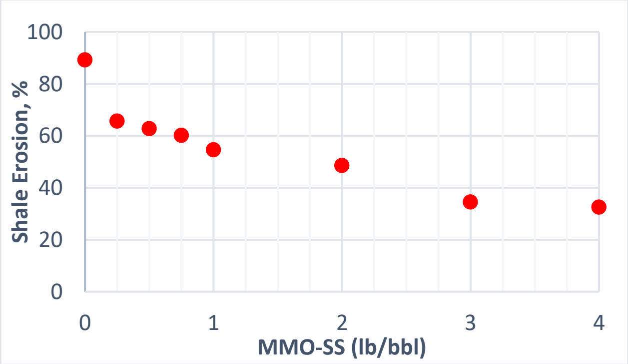


Figure 9. Percent Shale Erosion of Pierre Shale vs. Concentration of MMO-SS in an MMO Fluid.

Figure 9 shows the increasing concentration, ranging from 0.25 to 4.0 lb/bbl, of MMO-SS in an MMO fluid contributed to lower shale erosion of Pierre shale. Table 6 shows the base fluid prepared. A sizable drop in erosion is noticed when only 0.25 lb/bbl is added to the system, with additional increasing concentrations corresponding to a decrease in the total shale erosion that occurs.

Additionally, fluids were prepared to compare fluid stability to anionic contamination, with and without MMO-SS being present in the system, shown in Table 7. The fluids were prepared and the samples hot rolled at 150°F for 16 hours, then rheologies taken. Afterwards, the samples were contaminated with lignite, pH adjusted to 12.0, and hot rolled again for another 16 hours at 150°F and tested again. The evaluation used 0.25 lb/bbl of lignite as the anionic contaminant. When the lignite is added to the base mud without MMO-SS, the system completely lost rheology. When added to the muds that contained 0.25 and 0.5 lb/bbl of MMO-SS, near-identical rheological profiles are obtained before and after the addition of lignite.

Table 6. Base Mud Used for Shale Erosion Testing and Lignite Contamination.

Additives	Concentration
Water (bbl)	0.609
Pre-hydrated bentonite (bbl)	0.333
Soda Ash (lb/bbl)	0.25
MMO (lb/bbl)	1.0
AS (lb/bbl)	1.25
Calcium Carbonate (lb/bbl)	20.0
Barite (lb/bbl)	44.07
Caustic soda (lb/bbl)	0.5
MMO-SS	**As Required**

Table 7. Rheology of an MMO fluid with and without MMO-SS After Hot Roll at 150°F, Before and After Addition of Lignite Contamination.

Rheology @ 120°F	Base Mud		Base + 0.25-lb/bbl MMO-SS		Base + 0.50-lb/bbl MMO-SS	
HR@150°F	-	0.25-lb/bbl lignite	-	0.25-lb/bbl lignite	-	0.25-lb/bbl lignite
600	158	7	78	75	100	112
300	147	4	64	56	83	94
6	51	2	28	13	36	38
3	50	1	27	10	35	33
PV	11	3	14	19	17	18
YP	136	1	50	37	66	76
10-sec Gel	40	1	29	18	37	28
10-Min Gel	64	2	42	23	58	30
pH	12.05	11.90	12.06	11.89	11.95	11.94

Conclusions

There has continued to be new developments and improvements with the mixed-metal systems over the last three decades. Improved product handling, ease of use, and reduction of cost has continued to help this novel system to be used in different high-risk areas all over the world.

The primary attributes of the system are:

- Lost-circulation prevention
- Suspension of cuttings, cement, steel
- Wellbore cleaning to reduce the formation of cuttings beds on high angle wells
- Low viscosity at the drill bit
- Reduced pressure losses
- Improved caliper logs
- Minimum formation damage
- Low environmental impact

Continued advances in MMO technology has allowed for the creation of products that significantly improve the system's viability in more extreme environments, as a robust water-based fluid with improvements tailored for:

- Increased high-temperature tolerance to 400°F and higher
- Tolerance of high hardness-ladened fluids
- Improved shale inhibition
- Better tolerance to anionic contamination

Acknowledgments

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Nomenclature

mg/L = milligrams per liter
MMH = Mixed-Metal Hydroxide
MMLHC = Mixed Metal Layered Hydroxide Compounds
MMO = Mixed-Metal Oxide
MMOH = Mixed Metal Oxy Hydroxide
PHPA = Partially-Hydrolyzed Polyacrylamide
rpm = revolutions per minute

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