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GRECIAN MAGNESITE

TECHNICAL REPORT
Magnesium oxide as an oil-field chemical

1. Summary

Oil-field operations are handled by dedicated departments of oil and gas companies or specialized subcontractors. These include preparatory works such as exploration, drilling, cementing and fracturing, testing/completion and oil/gas production. These works are assisted by a variety of fluids and hundreds of chemicals. Main fluid mixtures are prepared on site by mixing independent raw materials and premixes with water or other fluids. The operations and applications involved are complex, require significant specialization and require significant technical know-how being a true craft.

Magnesium oxide is used in a large variety of sub-applications in the oil-field. The term *drilling fluids* is used to describe the application, but this is in fact a misnomer since this is just one aspect of the application. No single magnesium oxide grade can be used for the whole range and to address the market requires multiple grades, both CCM and DBM. In general, the requirements are quite diverse and the approach to the market must be on a case-by-case basis.

The following table summarizes the sub-applications, the requirements and the grades offered as well as some initial recommendations from our portfolio. More details are given in the next section.

Table 1. Application vs MgO grade summary

Sub-application	Known Requirements	Suggested
Clay activator/viscosifier (see 2.1.1)	CCM	ActiveMag 85 -75 to -150 μm
Alkalinity agent (2.1.2)	Various. Fine and High SSA for clay-free viscosifier systems	ActiveMag 85, ActiveMag 92 DF
Bridging agent (2.1.3)	CCM & raw,	ActiveMag 85, R5
Crosslinking agent (2.2.1)	Controlled reactivity HB, DBM	SM 94 DF
Gel breaker (2.2.2)	DBM, controlled BD	SM 94 DF
Cement expansion additive (2.3.1)	DBM, 3,1-3,3 g/cm3, 98% MgO, %hydration/expansion	SM88, SM94 DF
Special cements (2.3.2)		SM 94 DF

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2. Applications

2.1 Drilling fluids

These are fluids of various types and compositions. They are mixtures of natural and synthetic chemical compounds in a water or oil base that aid the drilling of boreholes. Their main roles are to cool and lubricate the drill bit, clean the hole bottom, carry the drill cuttings to the surface, control geologic formation pressures, control corrosion by adjusting pH and prevent liquids or gases present in the surrounding geologic formation from entering the well bore. The drilling operations are typically related to oil and gas production but could also be simpler operations such as water drilling. Drilling muds are a special case of drilling fluids used to drill most deep wells that have a thick consistency (*mud*).

2.1.1 MgO as activator/viscosifier of Clay slurries

Clays are essential components of drilling fluids due to the high viscosity and swelling they impart. Their characteristics and properties, especially bentonite's, are well defined by API and EN ISO 13500 standards (specifying minimum viscosity, degree of swelling and tendency to loose water by filtration). Lower quality bentonites may not meet the above standards and require "activation" (i.e. viscosity increase) by the addition of an alkali (typically sodium carbonate). CCMs from low to high reactivity have been reported in the literature as an alternative drilling fluid activator to sodium carbonate, or even having a synergistic effect with sodium carbonate or sodium aluminate. Viscosity increases (gelation) due to pH adjustment and MgO particle interaction with clay particles. CCMs show a stronger gelation effect than hard-burnt MgOs.

While in the past we thought that most of the "drilling fluid" applications mentioned by customers belonged in this category, the current survey found no clear proof of widespread use MgO as activator by related companies.

2.1.2 MgO as Alkalinity agent/pH buffer

This consists in fact of several similar applications, but treated here under one category, because customers may address multiple applications with a single product.

Alkalinity agents help provide fluid stability, improve polymer hydration and performance, and treat out contaminants like cement, carbon dioxide, hardness, and H_2S encountered in mix waters or while drilling. The chemicals of choice are hydrated lime, caustic soda, sodium carbonate, sodium bircarbonate and caustic calcined MgO.

Firstly, MgO can act as viscosifier/stabiliser in clay-free drilling fluids (i.e. those containing cellulose derivatives, gums or polymers such as polyamides or lignosulfonates). MgO will help the polymer to

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absorb water more quickly to thicken the fluid and impart stability over time, especially at increased temperatures. It is assumed that all this is accomplished due to pH adjustment.

Another application that falls under this title is the anti-microbial growth agent.

Finally, note that under the "pH-buffer" category can also be used for most other applications mentioned in the current report, since in most cases, the mechanism of MgO action is through pH adjustment. This could create confusion in properly identifying the application and the suitable grade or even the type (CCM or DBM).

2.1.3 MgO as Bridging Agent in Drill-in fluids

Drill-in or servicing fluids are special fluids designed exclusively for drilling through the reservoir section of a wellbore, typically horizontally. It is typically a brine containing only selected solids of appropriate particle size ranges (sized oxides or carbonates) and polymers (starch, xanthan gum or cellulose). This fluid must have the ability to deposit a "filter" cake on the walls of the well bore and prevent the drilling fluids and solids from being lost into the formation. After the drilling operation, the filter cake must be removed by use of clean-up solutions which may include strong mineral acids. MgO and $MgCO_3$ are reported in the technical literature as bridging agents, but no information is given on the required grades. Although it can safely be assumed that these need not be high grades, the MgO is probably a CCM, relatively coarse but there could also be special sizing requirements to minimize fines. Insoluble content may need to be restricted (i.e. low SiO_2 requirements) depending on the application.

2.1.4 MgO as Clay and Shale inhibitor

The water of the drilling fluid may interact with the geological formation (esp. if it is of the shale type and/or contains clays) and cause swelling and wash-out creating problems during drilling. MgO is mentioned as an inhibition agent preventing such interactions. We have not found the exact mechanism (although there is mention of MgO along with a phosphate forming a "geopolymer"), possible MgO specifications or specific commercial products containing MgO.

2.2 Hydraulic fracturing fluids

Hydraulic fracturing (aka fracking) is a well stimulation technique in which rock is fractured by a pressurized liquid. The process involves the high-pressure injection of 'fracking fluid' (primarily water, containing sand or other proppants suspended with the aid of thickening/gelling agents or gellants) into a wellbore to create cracks in the deep-rock formations through which natural gas, petroleum, and brine will flow more freely. Alternatively, fracking fluids can also be based on hydrocarbons or gas foams. When fracturing is completed, the thickness of the fluid must be lowered in order allow the proppant to deposit in the cracks to keep the formation open when fracturing pressure is released and thus enable efficient

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oil or gas production. This happens with the use of "gel breakers" – special compounds depending on the system, which are included in the fluid from the start but exhibit a delayed "breaking" action.

2.2.1 MgO as delayed crosslinking agent in Cross-linked water fluids

These fluids comprise 85-90% of the conventional wells that are fractured. They consist of water, proppant, gellant, a crosslinker and a breaker. The gellant is typically a guar gum which requires the use of borate salt to act as a crosslinker to maximize thickening (crosslinking creates a highly viscous gel). The fluid is initially slightly acidic and no cross-linking takes place, keeping the viscosity relatively low to allow the fluid to be pumped all the way down to the formation. However, the pH is constantly being raised at a controlled ratio to achieve thickening when the fluid reaches is destination (at pH of around 9,5). This delayed pH elevation can be achieved with the incorporation of MgO in the fluid. No MgO specifications have been found but since the application brings leather tanning to mind, a DBM of adjusted bulk density and granulometry could be suitable.

2.2.2 MgO as gel breaker in Hydrocarbon based fluids

Hydrocarbon-based fluids may be used for various purposes. These consist of a hydrocarbon base (frac oil, propane or LNG) gallant system and a breaker. Depending on the gel system (e.g. ferric sulfate/phosphorous acid), the breaker used can be a DBM. The action is also delayed here, like the cross-linked water application, but with the opposite effect, that of gradually decreasing the viscosity of the fluid.

2.3 Oil-well cements

Primary cementing fixes the steel casing to the surrounding geological formation. The casing is a large diameter pipe that is assembled and inserted into a recently drilled section of a borehole. Secondary cementing (*squeezing* or *plugging*) is used for filling formations, sealing and water shut-off. Cements are either Portland or special types. These cement systems are designed for temperatures ranges from below freezing in permafrost zones to 350°C in thermal recovery and geothermal wells. They also encounter pressures ranging from ambient to 200 bar. Accommodation of such variations in conditions was only possible through the development of cement additives.

2.3.1 MgO as Expansion additive

Portland cements suffer volumetric shrinkage upon hardening. The addition of expansion additives provide a net expansion effect which ensures good bonding between cement and casing, increased shear strength and zone isolation. Hardburned CCMs and DBMs are used as expansion additives, especially in high temperature applications (80, 120 or more than 150 °C). According to the technical literature, the MgO must not be reactive; it should exhibit slow hydration and not start expanding before the cement has set, because the net effect will be no expansion. In this respect, standard and heavy-burned DBMs achieve the best expansions (2-5%). Addition rates can go up to 10% per cement weight.

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Reported grades are 87% and 90% natural DBMs milled to around -200 μm and having bulk densities between 3.1-3.3 g/cm^3 or higher.

2.3.2 Special, non-permanent sealing cements

These are Sorel based formulations and are used at given areas to establish a seal and subsequently remove it by dissolving the cement with common oil-field acids, something that cannot be accomplished with conventional cements.