

# Technology Update

## New Environmentally Friendly Frac Fluid Developed for Offshore Applications

In recent years, the development of completion fluids for use in offshore wells has taken on a new component, namely that of satisfying new and pending environmental requirements.

Fracturing fluids typically are made up of the following chemicals.

- Bactericide to control bacteria growth.
- Guar-polymer viscosifying agent.
- Buffers to adjust the pH of the fluid to the desired pH for gel hydration and crosslinking.
- Borate salts to provide for either a surface or delayed crosslinking of the guar polymer.
- Breaker systems to reduce the crosslinked and base-gel viscosity back to 10 cp or less. (Internal breakers are liquids that stay with the fluid either in the proppant pack or the formation to break the gel, while encapsulated breakers usually provide a delayed break and become concentrated in the gel filter cake on the formation face and in the proppant pack to enhance the gel break.)
- Surfactants to prevent emulsions in oil wells, reduce surface tension for enhanced cleanup in gas wells, and stabilize clays.

In response to these challenges, an environmentally responsible fracturing fluid was formulated that performs equal to other guar/borate fluids in offshore environments. Through a systematic search of new and different chemistries, additives likely to ensure predictable performance across the fluid's temperature range were identified. Performance-predictability requirements included base-gel and crosslinked viscosity with the fluid's surface and delayed crosslinkers; low friction pressure to reduce hydraulic horsepower requirements; and proppant transport to carry the proppant through the surface-mixing and pumping equipment, the workstring, and throughout the fracture. The fracturing fluid also must resist shear degradation experienced while pumping and provide a predictable and controlled break.

The new B<sup>9</sup> Emerald FRAQ system, developed by Baker Oil Tools, passes the regulation for hexane-extractable materials for oil and grease as determined by U.S. Environmental Protection Agency (EPA) Method 1664 Revision A, along with mysid-shrimp toxicology limit of 30,000 ppm. Additionally, biodegradability is above the minimum Organization of European Cooperative Development requirement of 60% in 28 days.

### Fluid Development

**Bactericide.** When formulating a fracturing gel, the mix water usually is treated with a bactericide when it is added to the stimulation vessel's holding tanks. The bactericide keeps bacteria from growing in the gel and degrading its viscosity to the point where it will not perform and potentially could introduce bacteria into the reservoir. The bactericide must be effective against both anaerobic and aerobic bacteria species.

Normal oilfield bactericides did not meet the requirements for the toxicity level for the new fluid. The solution was in finding bactericides with appropriate half-lives to allow the water-holding

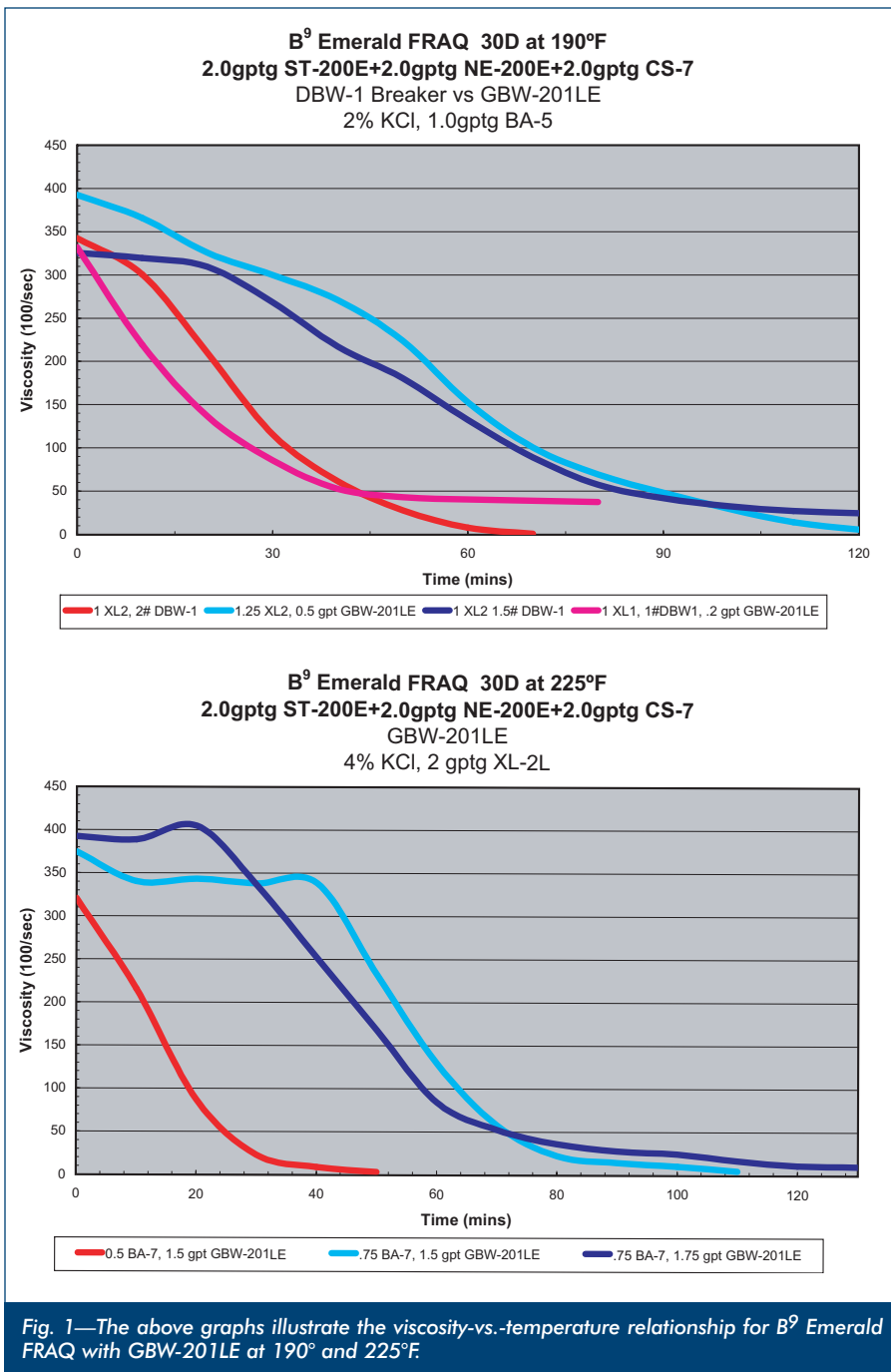
tanks to be treated, kill the bacteria, and then decompose before fluid discharge. The desired bactericide was found in the food and cosmetic industries. It has a predictable half-life that allows the holding tanks to be effectively treated when water is initially brought aboard. The selected chemical also has a high pH that functions as gel stabilizer in high-temperature applications.

**Viscosity.** Viscosity is built into the fracturing fluid by adding a liquid guar-polymer suspension to the treated water in a continuous process. Guar-polymer systems have been in use for more than 20 years and provide a uniform base fracturing fluid that usually is free of unhydrated gel lumps known as "fish eyes." Previous suspension systems were based on mineral oil. However, making the new fluid as environmentally benign as possible required it not only to be oil-floating and grease-free, but also to have low toxicity and to be biodegradable while suspending the guar polymer without settling. Systems formulated with various glycols proved to be the most promising, suspending 3 to 4 lbm of polymer per gallon of suspending agent. By eliminating the mineral-oil-base suspensions, the oil and grease content of the fluid was substantially lowered.

Initial field testing encountered substantial problems because the guar-slurry concentrate behaved as a dilatant fluid, increasing in viscosity under shear. This meant that it was easy to mix in the tote tanks under low shear, but when it came time to pump the initial formulation, it thickened and packed off in the metering lines and pumps. The problem was solved by adjusting the surfactant wetting agents and the concentration of the guar polymer, increasing the diameter of the metering lines, and increasing the pump size. Guar-polymer systems require two pH ranges for optimal performance. Initially the pH should be low, pH 6 to 7.5 for polymer hydration. Above this pH, the polymer is slow to hydrate, increasing the capacity of the gel-hydration tank for on-the-fly mixing. Normally, 3 minutes of hydration time is required to reach greater than 95% base-gel viscosity. After hydration, the fluid requires a pH above 8.5 for the borate crosslinker to work. At high bottomhole treating temperatures, the pH may need to be at or above 11.0 for the fluid to maintain the desired viscosity.

**pH Buffers.** The initial addition of the high-pH bactericide requires the addition of a low-pH buffer to facilitate gel hydration. Laboratory testing determined that a low-pH buffer could be added at the same time as bactericide addition while maintaining bactericide activity. On the basis of test results for oil and grease toxicity and biodegradability, the existing high-pH buffers met the environmental requirements.

**Crosslinkers.** Two crosslinkers, surface and delayed acting, were used to crosslink the guar polymer. Meeting the toxicity requirements required that the delayed breaker be reformulated. The delayed breaker is a finely ground borate-ore material suspended in a carrier fluid. In this case, the carrier fluid required reformu-



lation using essentially the same suspending agent used to build the slurried guar-polymer concentrate. Field testing determined the optimum borate concentration to overcome the problems discussed above with the slurried guar-polymer concentrate. The borate ore slowly dissolves with time and temperature to release the borate ion to crosslink the guar polymer. It can be used in conjunction with the surface crosslinker, nondelayed, to impart the desired surface and downhole viscosities. The selected borate crosslinkers function in deepwater applications in which fracturing fluids experience a cool-down/warm-up cycle as the fluid travels down the riser to the mudline. Most frac-fluid crosslinkers are designed to start reacting as the fluid goes downhole and is heated with the Earth-temperature gradient. Both the new non-delayed and delayed crosslinkers improved the crosslink-time

were replaced with aqueous, benign materials.

### Field Applications

In September and October 2003, the first three frac-pack treatments using the new fracturing-fluid system were performed in two gas wells (South Marsh Island Block 33 D-9 and Main Pass Block 289 C-31) and one oil well (South Marsh Island Block 33 D-12) for Apache in the Gulf of Mexico. The fluid system was mixed and pumped from stimulation vessels using standard mixing procedures and equipment configuration. The tip-screenout treatments gained from 500 to more than 1,000 psi net pressure. The wells produced as well as or better than expected, with one completion having less than 100 psi drawdown across the sandface.

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predictability for the fluid across its entire operating range.

**Fluid Breakers.** A new suite of fluid breakers was required because the standard breaker for guar-based fluids, the strong oxidizing breakers, could not meet the 30,000-ppm toxicity requirements specified by EPA 40 CF4 Part 435. These new breakers used a chemical approach for breaking the cross-linked and base polymer gel based on technology used in the food and baking industry. One of the patented breakers has shown excellent performance in the temperature range between 160 and 225°F (70 to 107°C). Most of the old-style oxidizers could not provide the desired break characteristics in this temperature range because of the nature of their chemistry. The new breaker, named GBW-201LE (Gel Breaker Water-Based-201 Liquid Environmental), functions well in this temperature range and thoroughly breaks the gel so that it will not recrosslink if cooled (Fig. 1).

**Surfactants.** Surfactants are added to fracturing fluids to accomplish a variety of functions such as preventing emulsions, water blockages, and foaming-while-mixing and improving fluid recovery after the treatment. Traditional surfactant products usually are formulated with a spectrum of organic solvents. Almost all of these had to be replaced in the new fluid because the original chemicals failed the toxicity and oil-and-grease requirements. Developmental efforts, therefore, centered on aqueous-based formulations. Most of the replacement surfactants came from the agricultural chemical industry. By using the varied facets of this technology, all of the necessary surface-tension reducers, nonemulsifiers, defoamers, and even clay stabilizers