# CLEARLY CLOUDY – FINDING A CLOUDING GLYCOL SYSTEM FOR FORMATE BRINES

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## Towards the perfect shale drilling fluid

Glycols or diols are a family of water-soluble alcohols containing 2 hydroxyl (-OH) groups. The simplest industrial diol is ethylene glycol, which is widely used as a coolant, heat transfer agent and anti-freeze fluid. A distinctive feature of glycols is that they become less water-soluble at higher temperatures and may eventually phase-separate from water as a very fine emulsion. The temperature at which this phase separation or 'clouding' occurs in aqueous glycol solution is known as the cloud-point temperature (CPT). This is determined by the amount of glycol in solution, the glycol's molecular weight and the concentration and type of salt in solution with the glycol. A change in any of these parameters changes CPT.

The addition of low concentrations (e.g. 1 – 5% v/v) of water-soluble glycols to water-based drilling fluids can improve drilling economics by:

- Maintaining wellbore integrity in shale sections – glycols slow down fluid invasion and pore pressure penetration in shale.
- Maintaining drilled cuttings integrity – glycols displace water from clay cuttings, reducing swelling pressure and maintaining cuttings integrity during their journey up the annulus. Polyethylene glycols (PEGs) are particularly good at intercalating within the clay matrix. Keeping cuttings firm and intact reduces mud maintenance costs and waste volumes.
- Lubricating contact surfaces – clouding glycols coat onto solid surfaces in their clouded state, providing good metal-to-metal and metal-to-rock lubrication in the wellbore.
- Reducing bit balling – glycols reduce bit balling and are widely used in water-based muds as ROP enhancement additives.
- Improving efficiency of filter cakes – glycols reduce drilling fluid loss rates and eliminate differential sticking at high overbalance.
- Slowing thermal degradation of polymer additives – glycols appear to reduce depolymerisation rates of fluid viscosifiers and fluid loss control polymers at high temperatures.
- Defoaming and demulsification – some glycols act as defoamers and demulsifiers, especially in their clouded state.

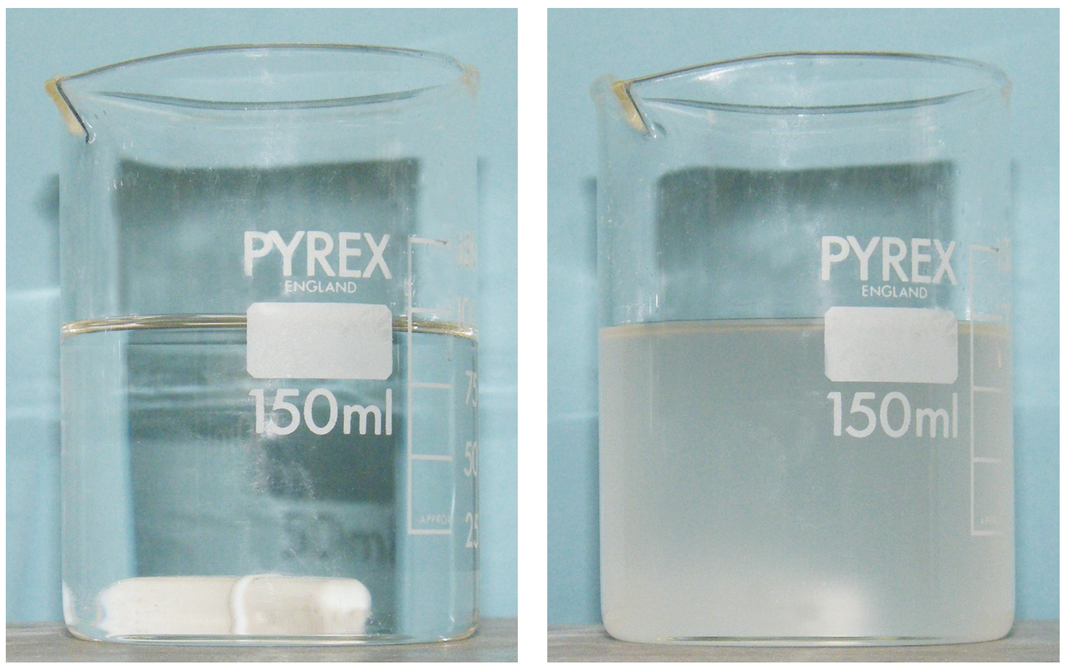



**Figure 1 1.85 g/cm³ cesium formate with 5% PEG 400 at room temperature (left) and heated to 60°C (right)**

Shell first tested clouding glycol drilling fluids, which are known as TAME (Thermally Activated Mud Emulsions) in 1992 by drilling over 30,000 feet of 17.5", 12.25", 8.5" and 6" holes in five deviated development wells and one exploration well in the UK North Sea. Shell's conclusion from its field evaluation of TAME (see SPE paper 26699) is:

***"The overall conclusion from this test campaign is that the TAME system is superior to conventional muds by virtue of its better borehole stabilising qualities, higher rates of penetration, significant waste reduction and lower mud time rates (i.e. the total time spent drilling on bottom, tripping, conditioning the hole or mud and circulating the mud)."***

Cabot and Formate Brine Ltd. have been developing a formate-based TAME fluid, seeking suitable clouding glycols that meet the following performance criteria.

- Low viscosity liquids at 25°C
- High flash points, i.e. > 70°C
- Thermally stable to 200°C
- Soluble to at least 5% v/v in potassium and cesium formate brines at 25°C
- Clouds-out in formate brines at temperatures of between 30°C and 200°C
- Non-toxic to humans and all other life forms that it might encounter
- Readily biodegradable

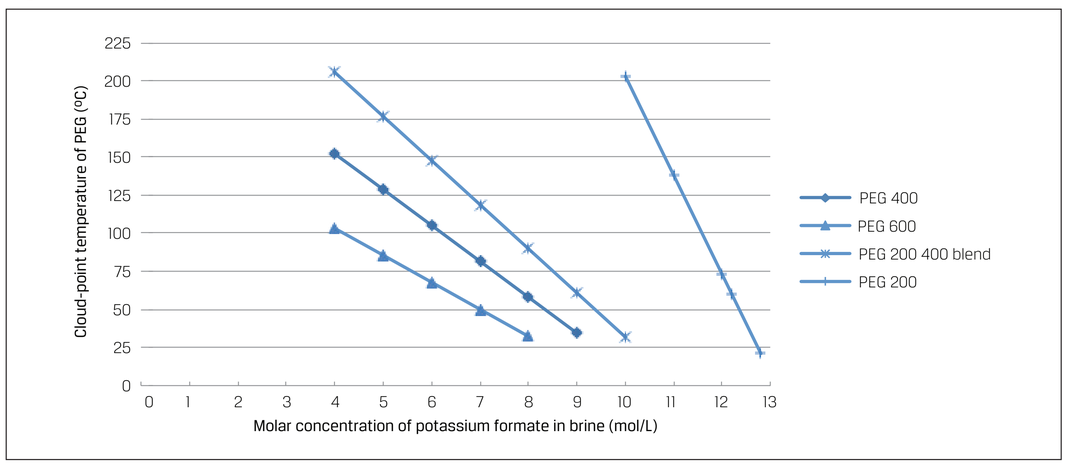
## Experimental

Initial screening identified polyethylene glycols (PEGs) in the molecular weight range 200 – 600 as good candidates for more detailed testing. The properties of PEG 200, 400 and 600 liquids are shown in Table 1.

**Table 1 Cloud-point measurements were made on 1 – 5% v/v solutions of these PEG liquids in potassium formate brines of 4 – 13 mol/litre and cesium formate brines of 2 – 11 mol/litre molarity.**

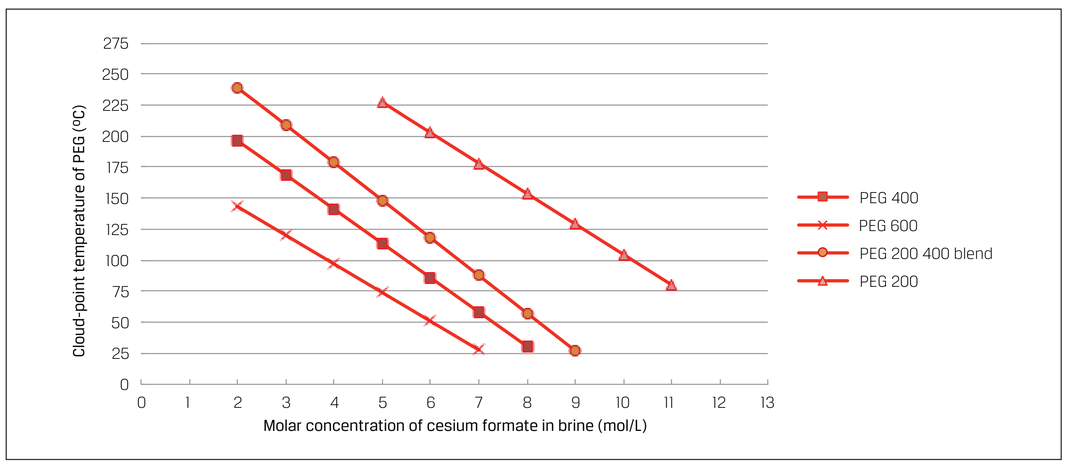
| Property | PEG 200 | PEG 400 | PEG 600 |
|---|---|---|---|
| **Viscosity @ 100°C (CSt)** | 4.3 | 7.3 | 10.8 |
| **Flash point, closed cup (°C)** | 185 | 227 | 185 |
| **Solubility at 5% in water @ 25°C** | Complete | Complete | Complete |
| **Freezing point (°C)** | -65 | 4 – 8 | 15 – 25 |
| **Density (g/cm³ @ 20°C)** | 1.124 | 1.125 | 1.126 |
| **Toxicity – human hazard** | Non-hazardous | Non-hazardous | Non-Hazardous |
| **Toxicity-environmental hazard** | Low toxicity | Low toxicity | Low toxicity |
| **Biodegradability** | Readily biodegradable | Readily biodegradable | Readily biodegradable |

**Figure 2 Cloud point of 5% PEG in potassium formate brine**




Figures 2 and 3 show cloud-point lines of the three PEGs and a PEG blend at 5% v/v concentration in potassium and cesium formate as a function of brine molarity. The lines are best fits of experimental data. These results indicate that selected PEGs in the molecular weight range 200 – 600 should be capable of creating active TAME-clouding glycol systems at any temperature between 25°C and 200°C in either cesium or potassium formate brines of 2 – 13 molarity (1.18 – 2.30 g/cm³ density).

**Figure 3 Cloud point of 5% PEG in cesium formate brine**




This preliminary work demonstrates that benign low-molecular-weight polyethylene glycols are effective clouding agents in high-density single-salt potassium and cesium formate brines. Further study is required to check PEG behaviour in mixed potassium/cesium formate brine blends with common drilling fluid additives.