Transition from oil & gas drilling fluids to geothermal drilling fluids

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Abstract

The harsh downhole conditions encountered in geothermal wells, specifically the high temperatures (HT) together with the toughness of the rock found in many geothermal formations, makes the drilling operation challenging. Drilling in such environments requires specialised drilling fluid formulations that have high thermal stability, good rheological properties, excellent lubricity and low formation damage. Given the wealth of experience in drilling wells in the oil industry, it is tempting to assume that the design of geothermal drilling fluids would be straightforward. However, is this the case? In this literature review, we have attempted to answer the question: "to what degree can developments in oil and gas drilling fluids be transferred to drilling fluids for geothermal wells?" To keep the scope of the review manageable, we have focused on two key aspects of drilling fluid design: rate of penetration (ROP) and HT fluid stability (and maintenance of the desired rheological properties of the fluid at high temperatures). The review has allowed the identification of gaps in both fundamental understanding and in existing technology. Rate of penetration is improved using low viscosity and low-density fluids, and we recommend that foams and aphron systems should be investigated to achieve this (depending on the application pressure). It should be noted, however, that such systems to date have only been studied at relatively low temperatures and the challenge of increasing the thermal stability of the formulation components needs to be addressed. Highly thermally stable polymer systems exist but these are both expensive and not widely available. A systematic study of the impact of copolymer molecular architecture on hydrolytic thermal stability is recommended. A promising solution to both maintaining good rheological properties at high temperature and providing fluid loss control is the use of particulates, especially those in the nano-size range. Additionally, nanocomposite systems show promise in this area and should be investigated. Particle stabilised foams and aphrons are a particularly interesting solution and we recommend that these are studied. It is also recommended to investigate the effect of drilling fluid on long term geothermal well performance.

Introduction

The number of geothermal energy exploration and drilling projects designed to access geothermal reservoirs has significantly increased in the last 20 years (De Angelis et al., 2011;

Reinsch et al., 2015; Kiran and Salehi, 2020;). One of the major challenges with developing geothermal resources is high drilling costs (Tester et al. 2006; William et al. 2008) Several studies have established that drilling costs can be up to 30% to 70% of the overall project cost (Lowry et al. 2017, Serdjuk, et al. 2013, Finger and Blankenship, 2012). There are many reasons for this. A principal cause is the harsh reservoir conditions encountered in many geothermal well drilling operations. Key challenges include issues related to fluid thermal stability, well control, well integrity, and lost circulation (Chemwotei, 2011; Finger and Blankenship, 2010; Kiran and Salehi, 2020). In addition to high temperatures, hard rock formations impose many technical limitations on selecting drill bits, casing materials, drilling fluids, and cement formulations. These conditions create the need for technological advancements to address HT challenges and rate of penetration issues (Finger and Blankenship, 2010). The HT conditions require the use of specialised drilling fluid formulations which have high thermal stability and can withstand high downhole temperatures, avoiding complications resulting from fluid degradation. The harsh conditions may also damage the casing, cement sheaths, and downhole tools. The most common type of formation rock in geothermal reservoirs are volcanic rocks such as granite, quartzite, granodiorite, and greywacke (Vollmar et al., 2013). These types of rocks are well known for their hardness, which is the resistance of the rock to being scratched, and abrasiveness, which is the ability of the rock to exert wear on metal tools. Both of these factors independently increase the wear on drill bits and shortens their life (Baujard et al., 2017; Finger and Blankenship, 2010; Miyazaki et al., 2019). As demonstrated by Bavadiya et al. (2017), the hardness of the rock is related to drill string vibration, resulting in the failure of downhole tools. Furthermore, the temperature variations in geothermal wells induce thermal stresses on the casing. When these stresses exceed the yield stress of the casing material, the casing fails owing to thermally induced stress fatigue (Shadravan and Amani, 2012; Teodoriu, 2015).

Geothermal wells are classified into three categories based on their temperature: low temperature (less than 150°C), medium temperature (between 150 and 200°C), and high temperature (greater than 200°C) (Kruszewski and Wittig, 2018). Furthermore, in some geothermal wells, the temperature can exceed the critical temperature of water, at which point the complexity of drilling and completion operations becomes more challenging (Bland et al., 2006; Kruszewski and Wittig, 2018). The actual temperature that the drilling fluid will be exposed to will be lower than the formation temperature owing to circulation of the mud from surface to the bottomhole and back to the top of the hole (Wang et al, 2023; Kahled, 2023). This can reduce the thermal stability requirements of the fluid considerably (by several tens of degrees).

The maintenance of drilling fluid properties under downhole conditions, throughout the drilling operation, is crucial. Variations in these properties should be mitigated to ensure efficient and cost-effective drilling (Bland et al., 2006). The elevated temperatures encountered in geothermal wells significantly affect the drilling fluid rheology (Ahmad and Federer, 2018; Fridleifsson et al., 2017). Although bentonite mud is commonly used in geothermal drilling, a substantial increase in the mud yield stress at elevated temperatures has been reported. This increase is attributed to clay swelling and flocculation at high temperatures and sodium ion substitution (Ahmad et al., 2018; Rossi et al., 1999).

Additionally, high temperature degrades polymeric additives present in drilling fluids and lowers the viscosity of the drilling fluid thus reducing its performance (Amani, 2012; Chemwotei, 2011; Kruszewski and Wittig, 2018; Lee et al., 2011; Sukhoboka, 2017; Tehrani et al., 2007). It was reported that high-pressure increases the viscosity and yield point of oil-based drilling muds by changing the volume of continuous phase owing to compression (Amani and Al-Jubouri, 2012a; Rossi et al., 1999). However, the impact of change in pressure on fluid properties such a viscosity is less than the effect of changes in temperature (this is intrinsic to the Clapeyron equation which describes the relationship of change in pressure and temperature on material properties) (Amani and Al-Jubouri, 2012b; Bybee, 1999; Davison et al., 1999; Sukhoboka, 2017).

In principle, the drilling operations of geothermal and oil and gas wells are similar (Bavadiya et al., 2019; Capuano, 2016; Saleh et al, 2020). However, in reality high temperature and pressure wells in the oil and gas industry are a niche market, which has led to a reduced research and development effort. To unlock geothermal energy with a focus on achieving net zero, a systematic study is required to understand the technical and scientific gaps in our knowledge and to identify any transferrable learnings from oil and gas drilling. This is especially true of drilling fluids used for drilling in high temperature environments. However, to date there has been no systematic study of the properties and behaviour of drilling fluids developed for high temperature (HT) oil and gas drilling operations compared with the technical requirements for geothermal drilling fluids. In this paper we attempt to address this gap by reviewing the literature to understand the requirements of a geothermal drilling fluid and compare these to the properties and behaviour of oil and gas drilling fluids. This has allowed us to identify the gaps in both fundamental understanding, in the existing technology and to elucidate the key technical challenges that remain.

Our analysis of the literature identified three main problems in geothermal drilling operation: 1. Poor rate of penetration; 2. Maintenance of optimal rheology at high temperatures (essentially maintaining a highly shear thinning fluid with sufficient low shear gel strength); and 3. The lack of fluids offering thermal stability beyond *ca.* 260 ˚C. Accordingly, the following review is divided into three main sections discussing rate of penetration and the impact of drilling fluid properties on this, polymer hydrolytic thermal stability, and the impact of solid stabilisers on fluid thermal stability. In the rate of penetration section, we identify solutions to this problem and suggest some research avenues. The polymer section discusses biopolymers separately to synthetic polymers and focuses on the properties that each monomer imparts to the final polymer attempting to identify the effect of the functional groups of the monomers on fluid thermal stability. We have attempted to identify and discuss studies that either have suitable laboratory data, or, ideally, field data illustrating the effect of the polymer on the thermal stability of the formulated fluid. The final section discusses the effect of solids as viscosifiers and fluid stabilisers. Since this is the more under-researched area, we identify gaps in knowledge and suggest avenues of research to improve our understanding of these materials.

Literature Review

Factors affecting rate of penetration (ROP)

The key questions that we tried to answer were:

1. What are the key parameters governing ROP?
2. Does ROP depend on rheology / composition of drilling fluid?
3. Can we make recommendations for new drilling fluid formulations to enhance ROP?

The area has been recently extensively reviewed by Najjarpour *et al* (2021, 2022a, 2022b). Historically, ROP management has mainly focused on analytical and semi-analytical models with several correlations being developed for this purpose. The key conclusions that can be derived based on the work of Najjarpour *et al* are:

1. The Bourgoyne and Young (1974) (B&Y) regression model is the most commonly employed model for ROP management, whilst that of Hareland and Hoberock (1993) is the second most used.

2. The B&Y equation, or a modified version thereof, is suggested by Najjarpour *et al* as the best choice when an analytical or semi-analytical model is required for ROP management.

3. ROP depends on the rheology / composition of the drilling fluid.

4. ROP increases linearly with decreasing plastic viscosity, solid content, and mud weight for both sedimentary and geothermal rock formations.

5. Artificial intelligence algorithms have been used in many ROP management studies This is because the prediction accuracy, in most cases, is good and the computing cost is low.

6. Several different machine learning (ML) approaches have been tried for ROP management with varying degrees of success. Many of the ML models are based on the B&Y model, but they do not include detailed drilling fluid properties – non-Newtonian rheology at HT, filtration (filtercake thickness / permeability), formation damage, etc. Promising machine learning approaches to rheological property prediction that could be coupled to ROP prediction are described by Davoodi et al. (2023c).

A key learning from the ROP literature is that ROP is increased when fluid viscosity and mud weight (essentially density) is decreased. However, in practice, a low viscosity might not be optimal at all times because for such factors as hole cleaning / avoiding cuttings sedimentation at low shear rate (or in quiescent state), a high viscosity is desirable (Caenn et al., 2017). Therefore, ideally a shear-thinning fluid is required. We discuss the consequences of this later in the paper.

High Temperature Tolerant Fluids for Oil and Gas drilling

High temperatures are a challenge in oil and gas drilling owing to the degradation of fluid properties, greatly reducing the ability to drill at high rate (Agwu et al, 2021; Gautam et al, 2022). In particular, the rheology of the fluid is significantly impacted under HT conditions. The cause of this is a combination of bentonite flocculation and the degradation of polymeric viscosifying agents (Kelessidis, 2009; Ali et al, 2020; Gautam et al, 2022). It is therefore challenging to maintain the desired equivalent circulation density (ECD) and viscosity since these both decrease as temperature increases. This impacts ROP and introduces considerable risk to the safety of the drilling operation (Maghrabi et al., 2011; Rommetveit and Bjorkevoll, 1997; Wang et al., 2012a).

HPHT additives: structure-property relationships

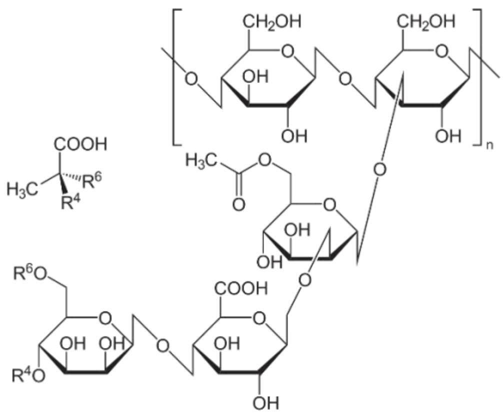
Various varieties of natural polymers, synthetic polymers, nanoparticles, and minerals have been frequently used as additives for drilling fluids. The performance of these additives depends on their structure and functional and physical properties. In general, these additives improve thermal properties of drilling fluids by acting as dispersants for bentonite preventing flocculation and by maintaining structural integrity at high temperature, thus maintaining the rheological properties of the fluid (Gautam et al, 2022).

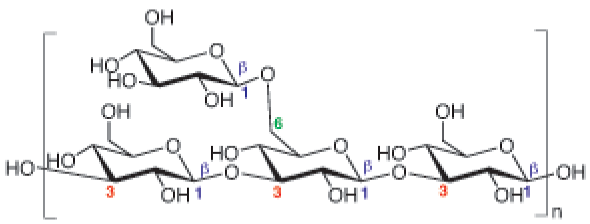
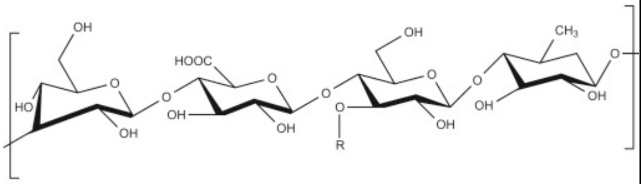
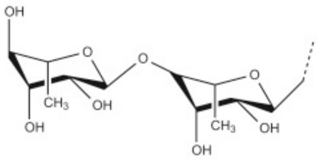
Polymeric Additives

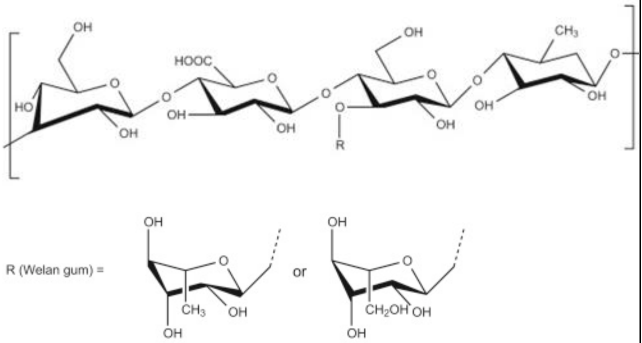
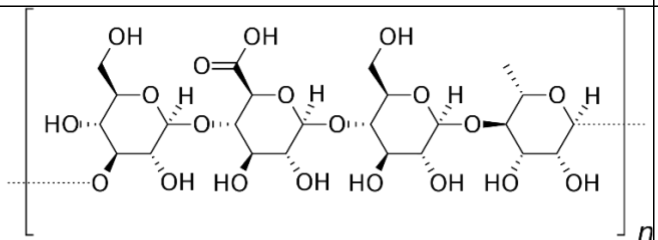
Polymers (natural and/or synthetic) are a common additive for HT fluid formulation in oil and gas drilling operations. The following sections discuss the range of polymers that have been tested and deployed.

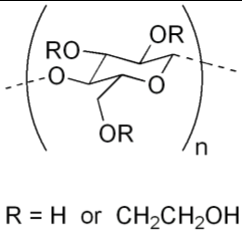
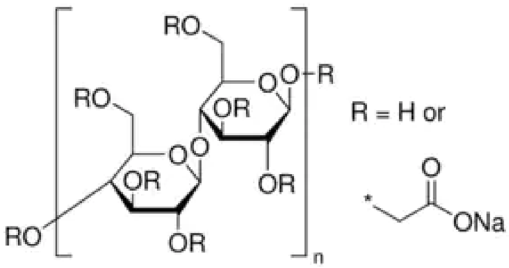
Bioploymers

Table 1 lists organic polymers that have been used in water-based drilling fluid formulations and lists the properties that the polymer imparts to the fluid.

Polymer	**Structure**	**Properties imparted**
Xanthan gum		Xanthan gum is a natural water-soluble high molecular weight polysaccharide produced by a fermentation process. Owing to its exceptional rheological properties (it adopts a double-helical conformation which leads to a shear thinning rheological profile), it is a very effective viscosifying agent for water-based drilling fluids (Caenn et al, 2017). It is environmentally benign (used as a food additive) but is temperature sensitive and loses its ability to viscosify fluids beyond 90 ˚C (Lambert et al, 1985).

Scleroglucan		Scleroglucan (also known as schizophyllan) is an extracellular polymeric substance of glucose produced by fungi. It is a high molecular weight, non-ionic polysaccharide composed of a (1,3)-β-d-glucopyranosyl backbone with (1,6)-β-d-glucopyranosyl residues as branches. It has better shear, salinity (non-ionic material) and thermal degradation resistance than xanthan gum. Its viscosifying behaviour is similar to xanthan and it is also environmentally benign (Kalpakci et al, 1990).
Diutan Gum	 R (Diutan gum) = 	Diutan gum is a natural high-molecular-weight gum produced by carefully controlled aerobic fermentation. The repeating unit is composed of a six-sugar unit. The backbone is made up of d-glucose, d-glucuronic acid, d-glucose, and l-rhamnose, and the side chain of two l-rhamnose. It adopts a double-helical conformation where the side chains screen the carboxylate groups of the backbone and prevent cross-linking by calcium ions. The rheological profile is shear thinning and it is more thermally

		stable than xanthan gum (Mota and Pereira, 2022)
Whelan Gum		Whelan gum is like Diutan gum, except that the side chains contain a single unit of either l-mannose or l-rhamnose. In aqueous solution. it adopts a double-helical conformation where the side chains screen the carboxylate groups of the backbone and prevent cross-linking by calcium ions. The rheological profile is shear thinning. It is stable above 90 ˚C (Benning et al, 2016; https://www.oceanviewchem.com/welan-gum.html)
Gellant Gum		Gellan gum is a water-soluble anionic polysaccharide produced by the bacterium *Sphingomonas elodea*. The repeating unit of the polymer is a tetrasaccharide, which consists of two residues of D-glucose and one of each residue of L-rhamnose and D-glucuronic acid. It exhibits a sol-gel transition in which there is a conformation change from random coil to double helix during cooling followed by aggregation of the double helices. The sol-gel transition temperature and gel strength of gellan gum depend on the cation

		species, polymer, and cation concentration. Compared to monovalent cations (K^+ and Na^+), divalent cations (Mg^{2+} and Ca^{2+}) can promote a more efficient gelation which is advantageous in a drilling fluid. The thermal behaviour is inferior to xanthan gum (Goa, 2015)
Hydroxyethyl cellulose (HEC)		Hydroxyethyl cellulose (HEC) polymer is a hydroxyethyl ether of cellulose, obtained by treating cellulose with sodium hydroxide and reacting with ethylene oxide. The polymer shows strong viscoelastic behaviour in aqueous solution (Ouaer and Mourad, 2018).
Sodium Carboxymethyl cellulose (CMC)		Carboxymethyl cellulose (CMC) or cellulose gum is a cellulose derivative with carboxymethyl groups (-CH2-COOH) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone (Caenn et al, 2017).

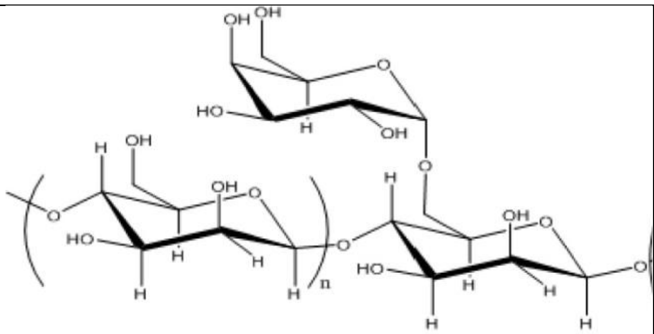
Guar Gum		Guar gum is a natural non-ionic polymer obtained from the annual agricultural crop Cyamopsis tetragonolobus, belonging to family leguminosae. Guar gum has been utilized as emulsifier, thickener, and stabilizer in the food and beverage industry and pharmaceutical chemicals in the pharmaceutical and cosmetics industry for a long time (Sharma et al, 2018). Nowadays, the petroleum industry is the biggest consumer of Guar gum and more than 40% of the world's Guar is used as additives in hydrofracking fluid (Hasan, A.M. and Abdel-Raouf. 2018)

Table 1. Organic (bio)polymers used in water-based drilling fluid formulations.

Unmodified natural polymers are not stable at the ultra-high temperatures often found in geothermal energy drilling operations (>200 ˚C) because of the low hydrolytic stability of the carbon-oxygen bond (acetal bond) found in the backbone of all of these polymers. Whilst the intrinsic bond strength of a paraffinic C-O is greater than a C-C bond, the high electronegativity of the oxygen atom makes the bond susceptible to nucleophilic and free radical attack with an OH leaving group. This is demonstrated by the low thermal stability of xanthan gum in aqueous solution (90 -120˚C; Lambert et al, 1985, Xie and Lecourtier, 1992). Of the natural polymers employed in drilling fluids, scleroglucan displays the highest thermal stability with an effective high stability of 135 ˚C (Kalpakci et al, 1990).

The thermal stability of natural polymers can be increased by functionalising them, by grafting them to synthetic polymers, and by forming polymer-inorganic composites. This is discussed later in this review. Additionally, the use of oxygen scavengers to reduce the concentration of oxygen to prevent corrosion helps with polymer stability under downhole conditions (Audibert and Lercoutier, 1993). This is because of the reduction in the concentration of free radicals of oxygen that attack the polymer backbone. This method is also effective for synthetic polymers (Zheng et al, 2020). The most common scavenging agents are erythorbic acid, sodium sulfite, and ammonium bisulfite (MacMohan et al, 2002).

Synthetic Polymers

The hydrolytic thermal stability of polymers is complicated and not without controversy (Vijayalakshmi and Madras, 2006; Oliveira *et al*, 2019). However, free radical attack at the backbone of polymers such as polyacrylamide in the presence of oxygen is a known pathway leading to chain scission and most probably the main route to degradation (Ma *et al*, 2015; Xiong *et al*, 2019; Vohlídal, 2020). This is illustrated in Figure 1 below.

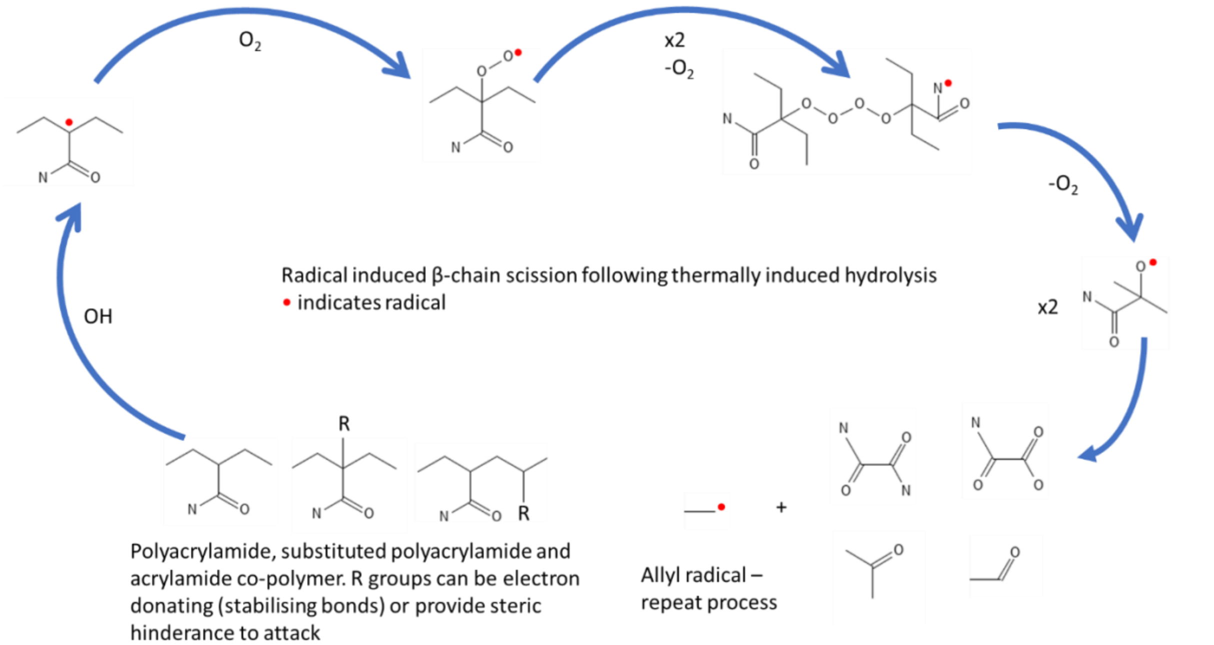


Figure 1. The Free Radical Route to Chain Scission in Polyacrylamide. In this Figure ^ denotes a radical.

In addition to polymer degradation, high temperature promotes polymer chain conformation changes that result in a loss of viscosity. At low temperatures the polymer chains are well hydrated and extended in solution allowing them to entangle and impart a high viscosity. As the temperature is increased, the chains can start to lose waters of hydration (that is the solvency of the water is reduced) causing the polymer to collapse and 'ball up' thus resulting in a loss of viscosity (De Gennes, 1979). This is illustrated in Figure 2 below.

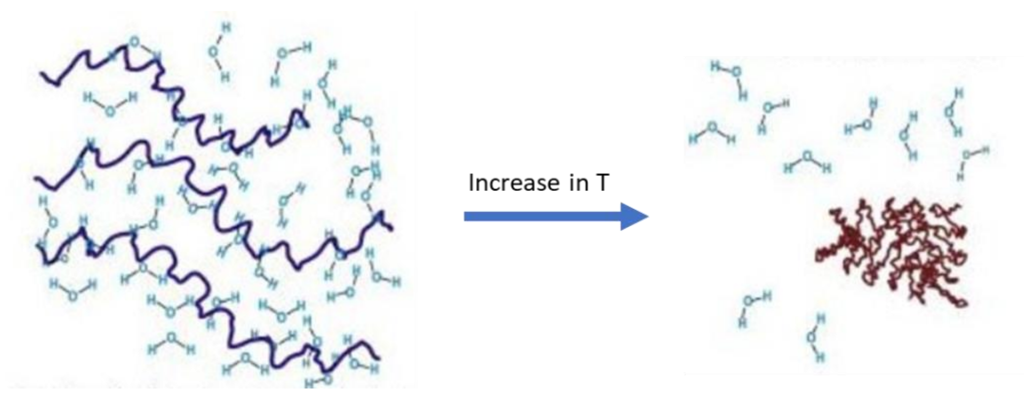


Figure 2. Cartoon illustrating the change in polymer chain conformation with increasing solution temperature.

This effect can be reduced by introducing co-monomers that protect hydrophilic groups or by imparting steric resistance to conformation changes (Gautam *et al.*, 2022; Davoodi *et al.*, 2023).

Finally, high temperatures can induce hydrolysis of the pendant amide groups in acrylamide-based polymers which produces carboxyl groups (Ma *et al.*, 2015). This can lead to precipitation of the polymer in saline waters through chelation with calcium ions and by crosslinking via cation bridges with a consequent reduction in viscosity and yield point.

These polymeric changes (degradations) have an impact on fluid rheology both directly and indirectly by a reduction in the ability of the polymer to disperse bentonite (particles through changes in adsorption capacity, changes in polymeric charge, and by chain length reduction). These effects all have impacts on key parameters such as ROP and the hole cleaning ability of the fluid. Figure 3 provides a visual summary of these effects.

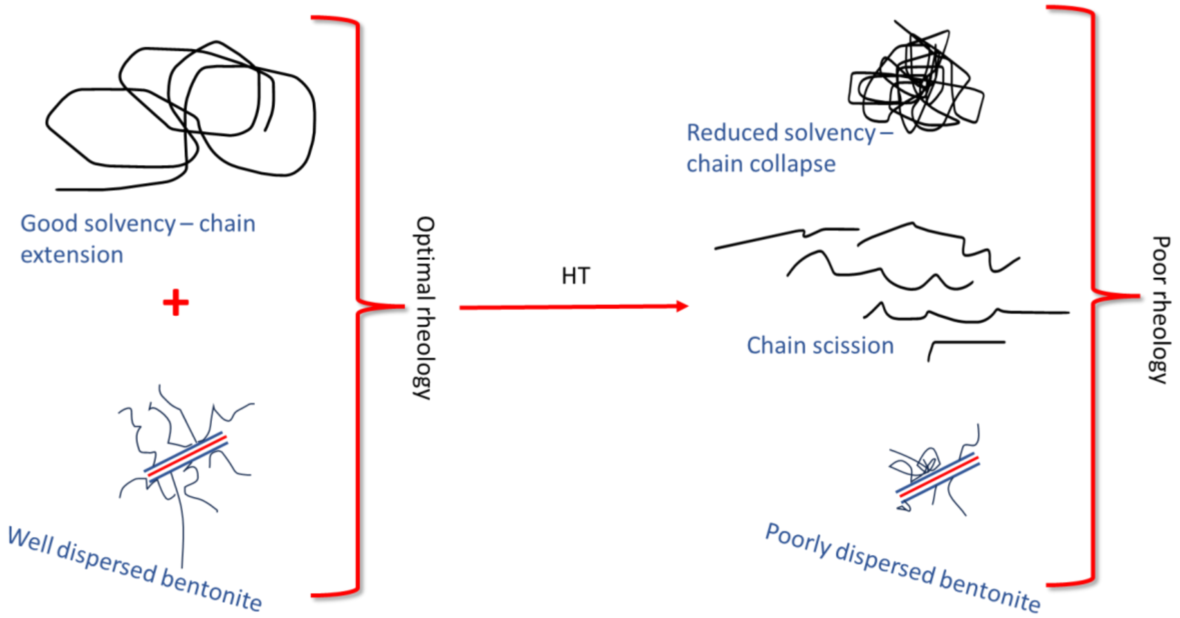
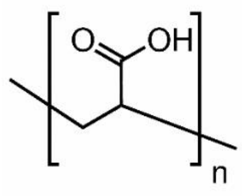
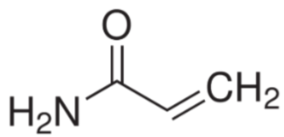
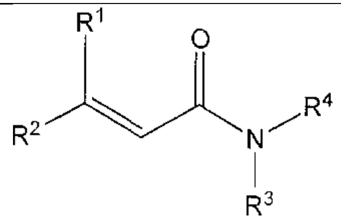
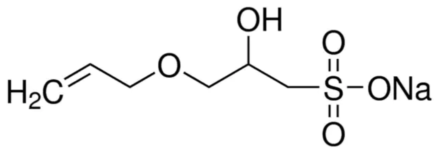
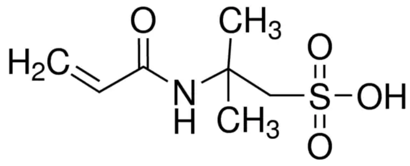
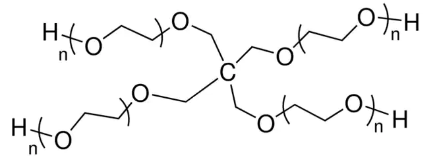
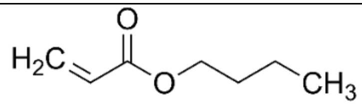
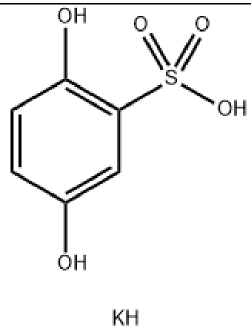


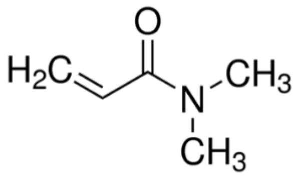
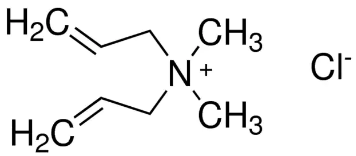
Figure 3. A summary of the impact of high temperatures on drilling fluid rheology

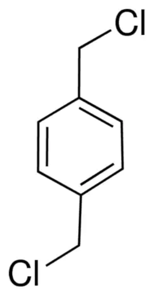
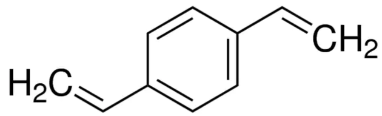
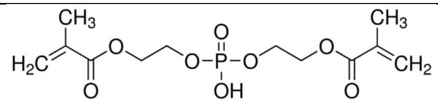
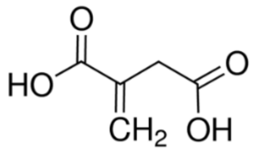
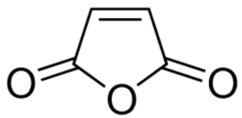
Table 2 lists the monomers that have been employed to make polymeric additives for drilling fluid use. The table lists the key properties imparted by the monomer to the polymer physical properties.

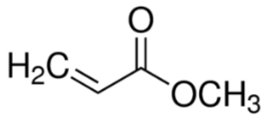
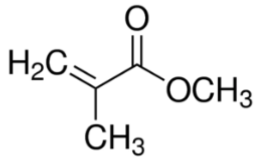
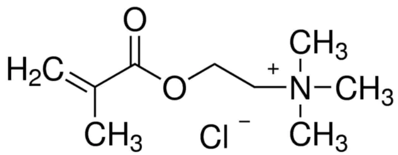
Polymeric monomer	Structure	Properties imparted
Acrylic acid (AA)		The carboxyl group provides a high degree of hydrophilicity to polymers containing this monomer and helps to maintain clay dispersion by forming intermolecular hydrogen bonds with clay platelets (Somiya, 2013). Furthermore, the high charge density imparted by the carboxyl group "shields" the polymers in high salt concentration brines preventing precipitation and loss of viscosity; it also improves stability in acidic pH (Sennakesavan et al., 2020).
Acrylamide (AM)		Acrylamide forms the basis of most water-soluble polymers used in industry. It is relatively cheap monomer and is highly reactive so simple to polymerise. In polymers, the acrylamide monomer displays improved dispersion of clays and acts as a viscosifying agent (Caenn et al, 2017)
Alkyl-substituted acrylamide (AAM)	 (II)	The amide group present in the monomer contributes to hydrophilicity of polymers containing this monomer and offers a site for hydrogen bonding, whereas the alkyl functional groups provide resistance towards

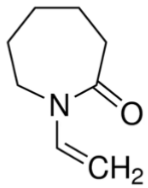
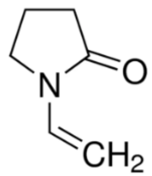
		alkaline hydrolysis of the polymer (Perricone et al., 1986)
3-(allyloxy)-2-hydroxy-1-propane sulfonic acid (AHPS)		The hydrophilic sulfonic acid group provides hydrolytic (and hence thermal) stability to polymers containing this monomer in high salt concentration brines (Sepehri et al., 2018)
2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS)		The combined effect of geminal dimethyl and sulfo-methyl group sterically hinders the reactivity of the non-ionic amide group (-CONH-) and imparts resistance of polymers containing this monomer to chemical decomposition (i.e., hydrolytic stability that enhances dispersibility and thermal stability). Furthermore, AMPS exhibits a high degree of hydrophilicity and anionic character at a wide range of pH, which is mainly owing to the presence of the sulfonic acid group in AMPS, and results in the enhanced water absorbing capacity with a high degree of water solubility (Jiang et al., 2019; Meng and Ye, 2017). Moreover, the sulfonic acid group in AMPS completely ionizes in aqueous solutions with a high ionization constant (Meng and Ye, 2017). As a result, it inhibits the precipitation

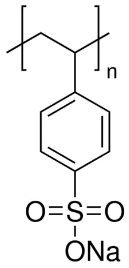
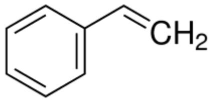
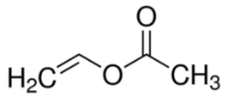
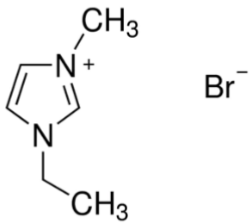
		of numerous cations, including calcium and magnesium, (Liu et al., 2003; Rivas et al., 2001). Therefore, AMPS containing polymers are the ideal additive for drilling fluids designed to be used in high salinity and/or HPHT conditions (Plank, 1992).
Allyl-polyoxyethylene ether (APEG)		The hydrophilic polyoxyethylene chains are reported to protrude in the aqueous phase and thus, impart steric repulsion and help control colloidal aggregation at high temperature and salinity (Liu et al., 2018).
Butyl acrylate (BA)		The vinyl and butyl-linked carboxylate ester groups in the monomer provides hydrophobic character to the associated copolymers and aids in thermal stability (Al-Muntasheri et al, 2008)
potassium 2,5-dihydroxy benzene sulfonate (DHBS)		The aromatic phenyl group provides rigidity to the copolymer, thus improving the thermal stability. The hydrophilic sulfonate group enhances the dispersion of bentonite by reducing the attraction between bentonite particles by electrostatic stabilization and plugging the filter cake holes (Peng et al., 2010)

N, N' dimethyl acrylamide (DMAM)		The unshared electron pair on the monomer promotes adsorption on clay surfaces. Furthermore, the non-polar dimethyl group promotes hydrolytic (and hence thermal) stability.in polymers containing the monomer (Nagre et al., 2016)
dimethyl diallyl ammonium chloride (DMDAAC)		The dimethyl group in the monomer provides steric hindrance to the cationic quaternary ammonium moiety (Wang et al., 2011b) and promotes hydrolytic (and hence thermal) stability of polymers containing the monomer. In addition, the DMDAAC monomer undergoes cyclic-polymerization leading to the formation of a new five-member ring pyrrolidine structure, improving the thermal stability of DMDAAC-containing polymers (Jia et al., 2019). The cationic charged quaternary ammonium moiety is absorbed by negatively charged clays (such as bentonite). The bond formed between quaternary ammonium and bentonite is stronger than the intermolecular hydrogen bonds, thereby enhancing the thermal stability of the drilling fluid (Lin and Luo, 2015).

α,α′ -dichloro-p-xylene (DPX)		The phenol groups provide rigidity to the polymer which improves thermal stability (Zhang et al, 2018)
p-divinyl benzene (DVB)		The rigidity of the phenyl group enhances thermal stability of polymers containing the monomer. Furthermore, the monomer can cross-link directly to other polymer chains, improving the thickening properties of the polymer (Xie et al., 2016)
Bis(hydroxyethyl methacrylate phosphate) (HEMA)		The pendant hydroxyl group imparts hydrophilic characteristics to associated copolymers and swells in water (Nagre et al., 2021)
itaconic acid (IA)		The two carboxyl functional groups present in the monomer give associated polymers a high degree of hydrophilicity) and aid the polymer at high salt concentrations under HPHT conditions (Teleky and Vodnar, 2019.
Maleic Anhydride (MA)		Maleic anhydride is an acid anhydride of maleic acid and exhibits hydrophilicity and highly anionic characteristics owing to the

		presence of two carboxyl groups. In addition, the heterocyclic furan improves the thermal stability of polymers containing the monomer (Lalehgani et al., 2019).
Methyl acrylate (Mac)		The carboxylate ester group in the monomer impart hydrophilic character to associated copolymers and aids in hydrolytic stability and dispersion. The pendant methyl group sterically shields the ester linkage and improves salt tolerance (Ali et al, 2015)
Methylmethacrylate (MMA)		The pendant methyl group in the monomer sterically shields the ester linkage from chemical attack (improves salt and calcium resistance) (Dodiuk, 2013) in associated polymers.
2-(methacryloyloxy)ethyl]trimethylammonium chloride (METAC)		The positively charged N+(CH3)3 group is strongly adsorbed onto the surfaces of clays and prevents the flocculation of clay particles. This helps in controlling the rheological and filtration characteristics of drilling fluids at HT conditions. In addition, the end methyl group imparts thermal and hydrolytic stability to the associated polymer (Xiping et al., 2016)

N-vinyl caprolactam (NVCL)		Polymers containing NVCL exhibit a lower critical solution temperature - at this temperature, the polymer undergoes a reversible phase transformation from the coil to the globule conformation (Kozlovskaya and Kharlampieva, 2019). In addition, the copolymers of NVCL undergo a ring-opening reaction when exposed to high temperatures resulting in the formation of a secondary amine structure on the backbone of the polymer. This leads to a greater molecular volume of polymer in aqueous solutions and increases the solution viscosity (Thaemlitz, 2006).
N-vinyl pyrrolidone (NVP)		The inelastic lactam group provides thermal stability to the polymer, and the vinyl group offers nucleophilic reactions with active-hydrogen-bearing functional groups. The amide carbonyl group is nucleophilic at the oxygen site, and this property enables the formation of intermolecular hydrogen bonds which improve dispersibility of clays. The presence of both hydrophilic and hydrophobic functional groups enhances the solubility of the polymer (Haaf et al., 1985).

sodium 4-styrene sulfonate (SSS)		The benzene sulfonate group imparts salt-resistant and high temperature stability to associated polymers and aids in clay dispersion. Furthermore, the aromatic benzene ring provides hydrophobic characteristics to the monomer and thus additionally improves the thermal stability of the associated polymer (Liu et al., 2020)
Styrene (ST)		The aromatic benzene ring provides hydrophobic characteristics to the monomer and thus improves the thermal stability of the associated polymer (Liu et al., 2020)
Vinyl acetate (VA)		The acetate group provides a high degree of hydrophobicity and thus, helps improve the thermal stability of VA-copolymers (Nagre et al, 2016)
1-vinyl-3-ethyl imidazolium bromide (VEIBr)		The imidazole structure exists in tautomeric form, and hydrogen can bond to any nitrogen atoms, making it highly polar with the electric dipole moment of 3.67 D. The rigid hetero-aromatic imidazole structure improves the thermal stability of associated polymers The cationic quaternary ammonium group improves calcium resistance by adsorption onto bentonite platelets (Christen et al, 1981).

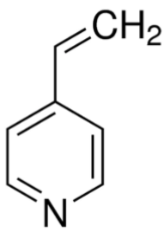
4-vinyl pyridine (VP)		The nitrogen centre of pyridine features a lone pair electron and thus, makes chemical properties like that of tertiary amines. Interestingly, the pyridine ring undergoes protonation to form a conjugate acid with an acid dissociation constant of 5.25 This behaviour helps control colloidal stability and filtration loss while drilling in high calcium (Ca^{2+}) concentrations and under acidic pH conditions (Pal, 2018).

Table 2. Monomers used to form homo and co-polymers used as drilling fluid additives in water-based fluids.

Two recent reviews have surveyed the use of synthetic polymers as drilling fluid additives (Davoodi et al, 2023a, 2023b) covering all functional aspect of the polymer in drilling fluids. Here we focus principally on the rheological properties of the fluid at high temperatures and specifically focus on the impact of different monomers and combinations of monomers on the thermal stability of the polymer.

Homopolymers

A homopolymer is a chain of chemically linked with identical monomer units. These polymers exist as flexible coils and are relatively easy to prepare and contain evenly distributed functionality throughout their backbone (Moerdyk and Bielawski, 2012).

Most industrial water-soluble polymers are based on acrylamide and acrylic acid polymers. These homo-polymers are then functionalised to improve or add performance to the polymer.

Polyacrylamide (AM)

Polyacrylamide is a water-soluble polymer formed by the polymerization of either acrylamide monomers or N,N′-methylenebis(acrylamide). In practice, the thermal limit for polyacrylamide containing drilling fluids appears to be up 150 ˚C (Alireza and Majid, 2013), although others have found a practical limit of ca. 90 ˚C (Borthaker et al, 1997) and can be lower in brines containing high concentrations of divalent ions (Omer, 2012). Silva et al. (2000) studied the thermal stability of polyacrylamide using thermo-gravimetric analysis (TGA) and reported that the thermal stability of polyacrylamide might be due to the presence of the hydrogen bonds present within the matrix. This also reduces the mobility of the polymer chain and therefore, increases the thermal strength. There is, however, a large disparity between the TGA thermal stability (300˚C) and the practical field-based stability (~90˚C). This is because the brine that dissolves the polymer acts to reduce the effectiveness of the polymer at providing viscosity to the fluid and controlling fluid loss.

Polyvinyl pyrrolidone (PVP)

Tehrani *et al.* (2007) developed a WBM system comprising of polyvinyl pyrrolidone (MW: 360, 000 Da), shale inhibitor (polyoxy-alkylene glycol), dispersant (Zirconium citrate), and weighing agent (Manganese tetroxide). The primary role of the polyvinyl pyrrolidone is as a high temperature deflocculant, owing to the nucleophilic amide carbonyl group that forms intermolecular hydrogen bonds. In contrast, the inelastic pyrrolidone functional group improves thermal stability. The formulation was found to be stable up to 356 ◦F (180 ˚C)) and relies on the synergism between weighing material and polymers to achieve stable and controllable rheological properties.

Poly(sodium 4-styrene sulfonate) (SSS)

Liu *et al.* (2020) studied the effect of poly sodium 4-styrene sulfonate (PSS) on the thermal stability of formulated WBMs. Poly(sodium 4-styrene sulfonate) is a homopolymer of sodium styrene sulphonate (SSS). It was observed that, with 1.0 wt% addition of PSS, the water-based drilling fluid remained stable at a temperature of 392 ◦F (200 ˚C). The PSS significantly reduced the aggregation of bentonite particles; this is attributed to the presence of a highly anionic sulfonate functional group that adsorbs onto the bentonite clay particles. In addition, PSS limits the coarsening of particles, resulting in stable rheology. The drilling fluid cake thickness and cake permeability were lower than those of drilling fluid without PSS, leading to effective control of filtration. Finally, the PSS-based fluid was used to drill an HPHT deep well in Xinjiang province, China, with a bottom hole temperature of 328 ◦F (165 ˚C).

Copolymers

A copolymer is a class of polymer formed when two or more different types of monomers are linked in the same polymeric chain. The goal of incorporating two or more monomers into a single polymer chain is to generate desirable physical and chemical properties that are not available with homopolymers (Scott and Penlidis, 2017). The macroscopic behaviour of a copolymer is significantly affected by the sequence and chain architecture of the comonomers. In addition to this, a copolymer may exhibit microstructural variations such as stereochemical isomerism and regioisomerism. Based on the chain architecture, a copolymer can be classified into linear, branched, crosslinked, and graft copolymers.

Linear copolymers

Styrene sulfonic acid-maleic anhydride (SSMA) copolymer

Chesser and Enright (1980) synthesized a low molecular weight copolymer (MW: 1000–5000 Da) involving sulfonated styrene and maleic anhydride. The functional groups (sulfonate) in the SSMA copolymer provide a high charge density which promotes adsorption on clay edges at elevated temperatures leading the clay particles remaining dispersed (preventing flocculation). In addition, the five-membered heterocyclic furan ring in maleic anhydride and the benzene ring of the SSS monomer improve the thermal stability of the copolymer. It is reported that the thermal decomposition of the copolymer was determined using thermos gravimetric analysis (TGA) and was found to be higher than 752 ◦ F (400 ˚C) (Chesser and Enright, 1980). The molecular arrangement of monomers in the copolymer favours steric hindrance, leading to stronger hydrogen bonding compared to higher molecular weight deflocculants (Chesser and Enright, 1980). The performance of SSMA polymer was evaluated in both the laboratory and the field. No fluid thickening was observed up to 500 ◦ F (260 ˚C), indicating the effectiveness of the additive as a high temperature deflocculant. In addition, the deflocculated state of the fluid at high temperatures improved the filtration performance. Although the SSMA performed satisfactorily in freshwater, the high electrolyte concentration of the seawater employed offshore had a detrimental effect on performance (Hille, 1985).

Audibert *et al.* (1999) reported the development of a novel polymeric filtration control additive comprising styrene sulfonate monomer. The polymer components were screened to optimize thermal stability, minimize rheological impact and limitations arising from formation damage due to fluid invasion. The developed additive was tested in a freshwater-based fluid, and no gelation of bentonite was observed after aging at 320 ◦ F (160 ˚C).

Vinyl sulfonate and vinyl amide (VSVA) copolymer

Lucas *et al.* (1981) developed a copolymer comprising of vinyl sulfonate (AMPS) and vinyl amide monomers, made using a solution polymerization technique. The copolymer enhances the formation of an impermeable filter cake after exposure to high temperatures, predominantly owing to the adsorption of polymer molecules onto clay particles; this hinders the penetration of water through the filter cake, effectively reducing filtration losses. Furthermore, owing to the presence of the sulfonate moiety, the copolymer offers enhanced salt tolerance. Son *et al.* (1987) investigated the thermal stability and electrolyte resistance of filtration control additives such as polyacrylate (PA), partially hydrolysed poly acrylamide (PHPA), and VSVA copolymer. It was observed that the vinyl backbone improves the thermal stability of the PA and PHPA copolymers. However, at a high pH value, the acrylamide group undergoes alkaline hydrolysis (Fieser and Fieser, 1961). Incorporating sulfonate groups in the polymer (VSVA copolymer) gives the polymer chains a high charge density and shields the acrylamide functional groups from saponification in a highly alkaline environment. The thermal stability and salt tolerance of VSVA copolymers-in a low clay content, low solid content, high electrolyte concentration drilling fluid were investigated. The VSVA polymer improved fluid stability up to 400 ◦ F (204 ˚C), retained good fluid loss control behaviour, and provided stable rheology properties.

Hille (1985) investigated the effectiveness of a VSVA copolymer under elevated temperature and high electrolyte concentration. The laboratory and field investigations revealed the effectiveness of the copolymer to control filtration properties up to 392 ◦ F (200 ˚C). The rheological properties of VSVA based fluids remained stable when contaminated leading to high concentrations of calcium and magnesium. This was due to electrostatic shielding of the acrylate groups by the anionic and highly charged sulfonate moiety. Apart from filtration and rheological improvements, the copolymer also minimized thermo-gelation. A well in North Germany with a bottom hole temperature of 383 ◦ F (195 ˚C) was drilled using VSVA treated saltwater fluid. The VSVA copolymer provided excellent stability to the drilling fluid, and no additional additives were required for 22 days of drilling.

AM-AMPS (AAM-AMPS) copolymer

Qu et al. (2023) synthesised an AM/AMPS copolymer and found that the plastic viscosity of the fluid after hot rolling at 464 ˚F (240 ˚C) was reduced by over fivefold. In contrast fluid loss performances was still acceptable. A previous study was more systematic. Perricone et al. (1986) synthesized two water-soluble copolymers of AM/AMPS and an alkyl-substituted acrylamide monomer (AAM) using an ammonium persulfate initiated bulk polymerization technique. The molecular weight of the copolymers ranged from 750 to 1500 kDa. It was reported that the amide and vinyl group could hydrolyse under alkaline conditions, whereas AAM provides resistance towards alkaline hydrolysis owing to the presence of the alkyl functional group (methyl, ethyl). The AAM/AMPS copolymer did not depolymerize under the hydrolytic and oxidative environment the drilling fluid was exposed to and did not form an insoluble salt in the presence of an electrolyte. The effectiveness of the copolymer was evaluated in a geothermal field with a downhole temperature exceeding 500 ◦ F (260 ˚C). Initially the drilling fluid employed used lignite and lignite derivatives; however, these were found to be uneconomical in controlling the filtration losses at elevated temperature. Therefore, the drilling fluid was treated with a copolymer to provide filtration stability. In another well, the copolymer was utilized to control the filtration loss occurring during a coring operation in a well with a bottomhole temperature exceeding 350 ◦F (177 ˚C). The copolymer

(AAM/AMPS) offered excellent core protection, and a permeability test indicated no formation damage.

Eisen et al. (1991) formulated a lime-based drilling fluid system comprising a VSVA copolymer and a low-molecular-weight polyacrylate terpolymer, lignosulfonate, and sulfonated asphalt to drill a well in Mustang Island, Texas, having a bottom hole temperature of 338 ◦ F (170 ˚C) The fluid was thermally stability up to 350 ◦ F (177 ˚C). Furthermore, the fluid also provided enhanced stability under salt and CO_2 contaminations.

Audibert and Argillier (1995) investigated the chemical modification of polyacrylamides to improve their thermal stability and the hydrolysis of acrylamide groups to acrylate groups by incorporating AMPS/SSS/MA monomers in the polymer. The authors also evaluated the stability of sulfonated polymers in a controlled environment. The study revealed that a typical sulfonate polymer starts degrading at a temperature higher than 302 ◦ F (150 ˚C).

Kar *et al.* (2011) reported formulation of high-performance water-based fluids comprising SSMA copolymer, AM-AMPS copolymer, and manganese tetraoxide (as dispersant, fluid loss control agent, and weighting agent respectively). The formulated fluid was reported to be thermally stable up to 392 ◦ F (200 ˚C).

Hydroxyl-sulfonated (HS) copolymer

Plank and Hamberger (1988) developed a synthetic sulfonated polymer comprising hydroxyl and sulfonic acid groups attached to the polymer backbone through alkene moieties. The low pka of the sulphonate groups prevents the chelation of calcium cations ensuring calcium tolerance greater than 200 g/L. The polymer containing drilling fluid was thermally stability up to 320 ◦F (160 ˚C). The copolymer was also reported to reduce the HPHT filtration losses of an offshore Gulf of Mexico well from 45 ml to 5.3 ml. The above-mentioned high temperature and calcium resistant hydroxyl-sulfonated polymer was further utilized in Zechstein wells in Germany. The polymer showed high electrolyte tolerance and was deemed cost-effective. It was also found that the polymer increased the thermal stability of additives such as lignite, starch, VSVA, and a polymer derived from cellulose (Ujma and Plank, 1989).

AA-AMPS copolymer

Wilcox and Jarrett (1988) investigated the effect of a polymeric deflocculant comprised of AA and AMPS comonomers on drilling grade clay and formation solids flocculation. It was reported that the polymeric deflocculant improved the thermal stability of the fluid, provided increased tolerance towards solids and electrolytes, and inhibited temperature induced gelation of the fluid.

Poly alkylene glycol

van Oort et al. (1997) proposed a new method to improve the thermal stability of conventional rheology modifiers and fluid loss control polymers by introducing polyglycols to the drilling fluid system. The authors evaluated three types of polyglycols: poly alkylene glycol, polyethylene glycol, and fatty amine ethoxylate. The hydrophobic association between the polymer chains and the polyglycol stabilized the polymer at elevated temperatures (320 ◦ F; 160 ˚C).

AM-NVP copolymer

Tehrani *et al.* (2009a, b) reported the formulation of a high-density HPHT water-based drilling fluid system comprised of clay and a terpolymer of AM, sulfonated monomer, and NVP. This fluid had excellent fluid-loss control properties and provided thermally stable rheology. A laboratory test indicated excellent fluid-loss control behaviour of the fluid formulation up to 450 ◦ F (230 ˚C). However, the fluid developed progressive gel strength, and therefore, the addition of a dispersant was required. Qu et al (2023) report a more than twofold reduction in plastic viscosity after hot rolling at 464 ˚F (240 ˚C) for a similar polymer. The authors state that the pyrrole ring groups, is effective in improving the stability of the polymer at high temperatures in aqueous solutions.

AM-SSS copolymer

Recently Qu et al (2023) have studied an AM/SS co-polymer-based fluid. After hot rolling 1t 464 F (240 C), the plastic viscosity was around half the room temperature value. It is postulated that the polymeric prevents bentonite flocculation because of its high adsorption on the clays thus stabilising the clay particles. Furthermore, the styrene sulfonate group imparts thermal stability to the AM backbone.

AM-DMDAAC copolymer

Lin and Luo (2015) synthesized a copolymer of AM and DMDAAC using ammonium persulfate-sodium bisulfite redox reaction to initiate free-radical polymerization. The copolymer was hydrolysed by treating it with sodium hydroxide. The thermal stability and salt resistance of the hydrolysed copolymer were evaluated by formulating freshwater and salt water-based fluids. The formulated fluid was thermally stable up to 392 ◦ F (200 ˚C) and had salt resistance up to 30 wt% of NaCl.

Star-poly[AM-AMPS]

Luo *et al.* (2018) synthesized a star-shaped copolymer of AM and AMPS using a multi-functional macro-initiator. The copolymer was prepared in a three-step process. The rheological and filtration performance of water-based drilling fluid formulated with synthesized copolymer was evaluated at 320 ◦ F (160 ˚C). It was observed that the copolymer-based fluid had better shear thinning behaviour and was more stable to high-temperature shearing.

Terpolymers

AM-AMPS- DI terpolymer

Wu *et al.* (2002) developed a terpolymer comprising di-sodium itaconate (sodium salt of itaconic acid), AM, and the sodium salt of AMPS using free radical polymerization. The terpolymer was used to formulate fresh and saltwater-based fluids. The prime function of the terpolymer was to act as a filtration loss control additive (by forming an impermeable filter cake) under high-temperature conditions (428 ◦ F, 220 ˚C)). In addition, the terpolymer behaved as a deflocculant. The stability of the saltwater-based fluid indicated a high salt tolerance capacity for the terpolymer at high temperatures. This is attributed to the carboxyl functional group of the DI monomer. The AM and AMPS improved clay dispersion, provided enhanced salt tolerance, and aided in the formation of an impermeable filter cake to minimize filtration losses at high temperatures.

AM-AMPS-VP terpolymer

Cao *et al.* (2017) synthesized a pH-responsive copolymer comprising AM, AMPS, and VP via ammonium persulfate initiated free radical polymerization. The comonomers AM, and VP acts as adsorption groups, whereas the AMPS units provide anti-calcium chelation properties to the copolymer. A freshwater-based fluid containing the synthesized copolymer and bentonite was found to be exhibit stable rheology and filtration control at 300 ◦ F (149 ˚C)) and was also found to be calcium resistant up to 20 wt%.

AM-AMPS- AA terpolymer

Peng *et al*. (2010) synthesized a terpolymer of acrylic acid (AA), and AMPS using a potassium persulfate–sodium bisulfite redox initiated free radical polymerization process. The synthesized terpolymer was evaluated by formulating fresh water-based fluids comprising bentonite and sodium bicarbonate. In addition, an aluminium citrate solution was also added to stabilize the fluid at elevated temperatures. A laboratory test confirmed improvements in fluid rheology and a decrease in filtration losses with the addition of terpolymer and aluminium citrate solution. The drilling fluid was found to be stable up to 356 ◦ F (180 ˚C). It was proposed that hydrophilic gels of low crosslink content are formed by the complexation reaction of the terpolymer and the aluminium citrate. The bridging of aluminium cations between the anionic terpolymer chains (which are negatively charged) and clay platelets helps inhibit the loss of viscosity typically encountered during high-temperature drilling.

AM-AMPS-VA terpolymer

Nagre *et al.* (2016) synthesized two acrylamide-based copolymers using a potassium persulfate-sodium metabisulfite redox initiated free-radical polymerization. The first copolymer (MWV: 4.75 × 106 g mol^{-1}) consisted of AM, AMPS, and vinyl acetate (VA) monomers (and was designated as CP4). The second copolymer (CP5: MWV: 4.56 × 106 g mol^{-1}) consisted of AM, sodium acrylate (NaA), N, N′ dimethyl acrylamide (DMAM), and NVP. The colloidal stability and salt tolerance of the synthesized copolymers at elevated temperatures was evaluated by formulating a freshwater-based fluid. The acrylamide-based polyelectrolytes enhanced the rheological properties of drilling fluid systems at temperatures up to 300 ◦ F (149 C)). The comonomer AM improves the dispersion of bentonite particles and acts as a bulk viscosifying agent, whilst AMPS provides hydrolytic stability and resistance towards salt contamination. The drilling fluid exhibited stable rheology in salt concentrations of 20 wt% NaCl, 2.0 wt% $MgCl_2$, and 2.0 wt% $CaCl_2$.

AM-AMPS-ionic liquid polymer

Yang *et al.* (2017) reported the synthesis of an ionic-liquid-based copolymer (PASV) via 2,2′ -azo-bis (2-methylpropionamidine) dihydrochloride (AAPH) initiated free-radical polymerization. The imidazole unit of the ionic liquid provides thermal stability, and the cationic quaternary ammonium group protects against calcium contamination. The other comonomer AM helps in rheological control at elevated temperature by increasing the thickness of the hydration layer, whereas the sulfonic group of AMPS helps in filtration and salt tolerance. The synthesized IL-based copolymer was evaluated for filtration loss control and calcium salt tolerance properties by formulating a freshwater-based fluid with calcium contaminates and thermally aging at 356 ◦F (185 ˚C). The copolymer was found to control filtration loss when aged up to 356 ◦ F (185 ˚C)) and calcium contamination up to 11 wt%.

AM-AMPS-SSS terpolymer

Huo *et al.* (2018) synthesized a terpolymer comprising of SSS, AM, and AMPS monomer through an inverse emulsion polymerization. The non-ionic amide units from AM and sulfonic acid groups from AMPS and SSS favoured adsorption on clay particles resulting in a well dispersed fluid system at high temperature. The formulated drilling fluid showed improved rheology at high temperature (arising from the phenyl group of SSS). The improved resistance to flocculation of the clay at high temperatures improved the filtration properties of the system. The rheological and filtration parameters of formulated copolymer-based fluid were not significantly affected by thermal aging at 320 ◦ F (160 ˚C). The micro-structural analysis revealed that the reduction in filtration losses was aided by physical plugging of the porous medium by the copolymer.

AM -AMPS -NVP terpolymer

Mao *et al.* (2020) synthesized an anionic polymer comprising AM, AMPS, and NVP using 2, 2′ -Azobis(2-methylpropionamidine) dihydrochloride (AAPH) initiated free radical polymerization. The polymer was used to formulate a water-based drilling fluid. The formulated polymer-based fluid was found to be resistant to chlorine and calcium ion contamination (resistant up to 4.5 × 105 ppm and 4 × 105 ppm, respectively) after thermal aging at 356 ◦ F (180 ˚C). Owing to the presence of the sulfonic acid group (AMPS monomer) and pyrrolidine group (NVP monomer), the synthesized polymer exhibited a stronger interaction with bentonite particles under high-temperature conditions leading to improvement in the colloidal dispersion f the clay in the drilling fluid.

AM-AMPS-VI (AAV) terpolymer

Aghdam *et al.* (2020) synthesized a polymeric fluid loss control agent comprised of monomer AM, AMPS, and 1-vinyl imidazole (VI) using radical polymerization in the presence of potassium persulfate initiator. The fluid loss control properties were evaluated by thermally aging a water-based drilling fluid containing AAV at 365 F (180 ◦C). The filtration loss volume was found to be in the range of 1.4 ml–6.5 ml with thinner filter cake in the range of 0.21 mm–0.79 mm. The fluid control mechanism of the AAV copolymer was attributed to the deflocculation of bentonite particles, surface adsorption onto bentonite particles and the formation of a chelate complex with cations.

Quadripolymers

AM-AMPS NVP-SSS- quadripolymer

Li *et al.* (2014a, b) synthesized a quadripolymer comprising AM, AMPS, SSS, and NVP via redox-initiated free radical polymerization. The quadripolymer was found to effectively control the filtration loss of a freshwater-based fluid when subjected to an aging temperature of 392 ◦ F (200 ˚C)). The high-temperature stability of the polymer is attributed to the presence of hydrophobic pyrrolidine and phenyl functional groups on the NVP and SSS monomers. Drilling fluid samples treated with salt to mimic fluid contamination showed reduced viscosity owing to aggregation of the polymer. However, filtration loss volume was unaffected, confirming a degree of salt resistance for the polymer. The filtration behaviour was attributed to the adsorption of the polymeric chains on bentonite in the fluid. In addition, the adsorption behaviour of polymer was characterized using AFM. The AFM analysis showed uniformly dispersed polymer on the bentonite surface with formation of a networked structure.

AM-AMPS-NVP-DMDAAC quadripolymer

Su *et al.* (2014) synthesized a quadripolymer comprising AM, AMPS, NVP, and DMDAAC using potassium persulfate-sodium bisulfate redox initiated solution free radical polymerization. This resulted in a polymer with an average molecular weight of 530 000 Da. The thermal stability and salt tolerance of the polymer were evaluated by formulating a salt saturated brine-based fluid. After thermal aging, the fluid showed stable rheology and filtration loss behaviour up to 356 ◦ F (185 ˚C). The fluid loss control behaviour of the polymer was compared with an AM-AMPS-NVP terpolymer. It was observed that the quadripolymer controlled fluid loss volume better than the terpolymer. The thermal stability of the quadripolymer is attributed to the incorporation of hydrophobic temperature-resistant pyrrolidine functional groups in the polymer (introduced by the NVP monomer). In addition, the DMDAAC monomer favours the formation of a pyrrolidine structure during polymerisation, thereby further increasing thermal stability. It is postulated that the quaternary ammonium group of the pyrrolidone inhibits the swelling of clays and hence improves the quality of the filter cakes formed leading to effective control of fluid loss.

AM-AMPS-DMDAAC-SSS quadripolymer

Bai *et al.* (2015) synthesized a quadripolymer comprising AMPS, AM, DMDAAC, and SSS via an ammonium persulfate initiated free-radical solution polymerization reaction. Monomers such as AMPS and SSS bear sulfonic acid groups which improve the salt tolerance of the fluid. The phenyl group from SSS provides rigidity to the polymer backbone and hence improves the thermal stability of the polymer. DMDAAC acts to inhibit flocculation of bentonite and hence improves the quality of the filter cakes formed leading to a decrease in filtration loss. The selection of the monomers was optimized using an orthogonal design of experiments approach. The rheological and filtration loss behaviour of the quadripolymer was evaluated by subjecting the formulated drilling fluid to thermal aging. The results indicated that rheological and fluid loss properties of the drilling fluid are stable up to 356 ◦F (180˚ C).

Huang *et al.* (2019b) reported the synthesis of a quadripolymer also comprising AM, AMPS, DMDAAC, and SSS made via free-radical aqueous solution polymerization. The thermal stability and salt tolerance behaviour of the polymer-based fluid were evaluated at HPHT conditions. It was observed that the polymer imparted stable rheology up to 464 ◦F (240 ˚C), and salt-resistance up to 30 wt% NaCl. The high-temperature stability is attributed to the phenyl and pyrrolidine structure of the quadripolymer. However, the polymer was not able to resist $CaCl_2$ contamination. The filtration control of the polymer was compared with commercial additives and was found to be more effective in controlling filtration loss.

AA-AMPS-MA-DMDAAC quadripolymer

Huang *et al.* (2015) synthesized a quadripolymer comprising AA, AMPS, DMDAAC, and MA monomers via ammonium persulphate initiated free-radical polymerization. The polymerization conditions and initiator dosage were optimally selected to obtain a low molecular weight quadripolymer (MWW: 8036 Da, MWN: 8107 Da). A freshwater based drilling fluid comprising sodium carbonate, calcium bentonite, clay, and quadripolymer was prepared to assess the thinning properties of the quadripolymer. The results were also compared with a commercial thinner. The quadripolymer was found to reduce the viscosity of the fluid up to 473 ◦ F (245 ˚C)). The viscosity reduction is attributed to the presence of cationic moieties (DMDAAC) and strongly hydrated groups (AMPS), resulting in polymer adsorption on the calcium montmorillonite (Ca–Mt), thus providing strong hydration and swelling inhibition.

AM-AMPS-SSS-METAC quadripolymer

Xiping *et al.* (2016) synthesized a quadripolymer comprising AM, AMPS, SSS, and METAC monomers using ammonium persulfate-initiated solution polymerization. The cationic quaternary ammonium and tri methyl end groups prevent clays from flocculating, and the sulfonic acid group (SO_3^- Na^+) from the AMPS and SSS monomers provides a high degree of hydrophilicity to the polymer and thus, improves salt tolerance. The resonance stabilized benzene ring of SSS imparts heat resistance to the polymer. The quadripolymer was evaluated by formulating a freshwater, a saturated saltwater, and a composite-brine drilling fluid. The API filtration loss was found to be 5.2 mL whilst the HPHT filtration loss at 392 ◦ F (200 ˚C) was found to be 10.6 mL, indicating effective filtration loss control.

AM-AMPS-NVP-DHBS quadripolymer

Chu and Lin (2019) synthesized a polymer (PAAND) comprised of AM, AMPS, NVP, and potassium 2,5-dihydroxy benzene sulfonate (DHBS) by introducing the phenyl group in the backbone of copolymer through horseradish peroxidase (HRP) mediated RAFT polymerization. The rheological and filtration properties of the copolymer-based fluid were evaluated by thermal aging at 464 F (240 ◦C). The efficiency of controlling rheology and filtration loss at high temperature was found to follow the order: PAAND > PAANS > PAAN copolymer. The incorporation of rigid DHBS monomer in the backbone of copolymer improved rheological stability and filtration control at high temperatures.

AM-AMPS-HEMA-LMA quadripolymer

Nagre *et al.* (2021) synthesized a hydrophobically associating heteropolymer (HAH) comprising AM AMPS), HEMA, and LMA using micellar radical polymerization. The monomer AM was selected to provide viscosifying behaviour to the polymer, whereas AMPS imparted a high anionic charge and offering temperature and salt tolerance. The monomer HEMA was added to increase the water retention capacity of polymer to decrease filtration losses. LMA provided allowed hydrophobic association in saline media and inhibited chain collapse. The filtration behaviour of a HAH-containing water-based drilling fluid was studied in the temperature range of 25–160 ◦C. The polymer maintained excellent filtration control with a fluid loss volume of 8.4–8.6 ml compared with 43.5–107.0 ml for polymer-free fluids. In addition, the salt contaminated fluid was also found to impart stable rheology with API filtration loss of 7.6–8.8 ml after hot rolling at 302 ˚F (150 ◦C).

AM–AMPS -NVP–IA quadipolymer

Wu *et al.* (2001) synthesized a copolymer comprising of NVP, IA, AM, and AMPS using free radical polymerization. A laboratory test of a formulated freshwater-based fluid comprising bentonite, sodium carbonate, and the synthesized copolymer, confirmed the excellent filtration control properties of the copolymer up to a temperature of 428 ◦F (220 ˚C). The high-temperature resistance of the copolymer is attributed to the cyclic pyrrolidone unit of the NVP monomer. In addition, the anionic sulfonate group binds with clay particles stabilising the clay and keeping particles deflocculated. The improved filtration behaviour was attributed to the large chain length of the polymer.

AM-AMPS-SSS-DMDAAC quadripolymer

Wang et al. (2022) synthesised a quadripolymer comprised of AM, AMPS, SSS and DMDAAC. The effect of hot rolling at different temperatures was studied and it was found that the viscosity of the formulated fluids was relatively stable up to 356 ˚F (180 ˚C), thereafter there was a considerable reduction in viscosity. At 428 ˚F (220 ˚C), the apparent viscosity was reduced by around 75%.

DMAA-AMPS-DMDAAC-NVCL quadripolymer

Li *et al.* (2022) report synthesising a zwitterionic quaternary copolymer comprised on DMAA, AMPS, DMDAAC and NVCL. After hot rolling a fluid containing the novel polymer at 428 ˚F (220 ˚C), the filtration loss of the fluid was only 6.5 ml. The apparent viscosity, in both the absence and presence of salt, was reduced by only around one third. The apparent viscosity was hardly impacted in the absence of but reduced by up to one third at the highest salt concentration (36%).

Branched polymers

AM-SSS-APET terpolymer

Yan *et al.* (2013) synthesized an amphiphilic comb-shaped terpolymer of AM, SSS, and allyl polyoxyethylene-12 ether (APET) using an inverse microemulsion polymerization technique. The amide and polyoxyethylene units of the terpolymer improved clay dispersion by forming intermolecular hydrogen bonds with clay particles and helped to develop a networked structure. The negatively charged sulfonic acid group improved the colloidal stability of fluid. It was proposed that the high hydration ability of the sulfonic acid groups inhibits damage to the hydration shell of the bentonite under high temperature and salinity conditions. In addition, the unique comb-like structure also favours the formation of networked structures and helps in the reduction of salt screening. For the evaluation of the polymer, a low solid drilling fluid comprising bentonite, sodium bicarbonate, and polymer was prepared and laboratory tested under high temperature and high salinity conditions., The zeta potential of the clay particles in an aged sample (at 302 F. 160 ˚C)) of the fluid was measured and found to be − 31.1 mV, indicating colloidal stability of the clay. Furthermore, the formation of a networked structure between bentonite and terpolymer ensured the formation of compact filter cake and low filtration volume under high temperature and salinity conditions.

AMPS- NVP-SSS- APEG terpolymer

Liu *et al.* (2018) synthesized a comb-shaped copolymer of AMPS, NVP, SSS, and allyl polyoxyethylene ether (APEG) by free radical polymerization. The APEG chains imparted steric hindrance and helped in controlling colloidal aggregation of clay at high temperatures and under high salinity conditions. The other comonomers, AMPS, and SSS offered an ionizable sulfonic acid group that increases the hydration shell around the clay particle and improves salinity tolerance. In addition, the ring structure from NVP and SSS monomers helped to enhance the rigidity of the main chain and improved temperature tolerance. The filtration control behaviour of the polymer was evaluated by aging the fluid at 392 ◦ F (200 ˚C). The fluid loss volume was found to be less than 10 mL, indicating the effectiveness of polymer in controlling fluid loss at elevated temperatures. The salt tolerance of the polymer was evaluated by adding variable loadings of salt contaminates to the fluid and thermal aging at 356 ◦ F (180 ˚C). A fluid loss volume of fewer than 15 ml was observed with a contamination of 10.0 wt% NaCl and 1.0 wt% $CaCl_2$, indicating excellent salt tolerance for the polymer.

Crosslinked polymers

Long linear polymers have limited tolerance to salt contamination and shear sensitive (i.e., can be degraded at high shear rates). Compared with linear polymers of similar molecular weight, crosslinked polymers have smaller hydrodynamic volumes. This property results in crosslinked polymer being sterically hindered which increases hydrolytic (thermal) stability (Thaemlitz et al., 1999). The smaller size of the polymer also makes them more shear resistant and the crosslinking makes the polymer less sensitive to solid contaminants.

AMPS-NVCL-DVB terpolymer

Xie *et al.* (2016) synthesized a copolymer (SDKP) comprised of AMPS, and NVCL monomers, crosslinked with di-vinyl benzene (DVB) using 2,2-Azobisisobutyronitrile (AIBN) initiated micellar radical polymerization. The synthesized cross-linked polymer was evaluated by formulating a low-solid freshwater base drilling fluid. The polymer displayed a thermo-thickening effect in a temperature range of 302–356 ◦ F (150–180 ˚C), providing good viscosity control and compensating for the thermal thinning of drilling fluids at elevated temperatures. The fluid was found to provide resistance towards elevated temperature up to 446 ◦F (230 ˚C) and salt tolerance up to 8.0 wt %.

AM-AMPS-AHPS-AA terpolymer

Sepehri *et al.* (2018) studied the effect of crosslinking agent, transfer agent, and co-monomer loading on the fluid loss and rheological properties of the resulting polymer. The first terpolymer (CP1) was synthesized by solution polymerization and consisted of AM, AMPS, and NVCL monomers. It was observed that the cross-linked polymer offered better fluid loss control than a linear polymer. However, it was also reported that cross-linker increased the viscosity and decreased the solubility of the polymer. Additionally, the effect of the chain transfer agent was also evaluated. It was found that an increase in chain transfer agent reduced molecular weight and viscosity; however, fluid loss volume was increased. It was also observed that an increase in AMPS content also increased fluid loss volume but increased salt tolerance. The AM units contain $–CONH_2$ groups that enhance interaction with bentonite to provide helping disperse the clay particles and improving the high temperature viscosity of the drilling fluid. The sulfonic acid group of the AMPS monomer provides salt tolerance. In addition, the rigid lactam group from NVCL improves the thermal stability of the polymer. The second copolymer (CP2) comprised AM, AMPS, AHPS, and AA monomers. The effect of CP1 & CP2) on thermal stability and filtration control was evaluated in a water-based drilling fluid. It was reported that CP2 led to lower filtration loss volumes than CP1 after thermal aging at 302 ◦ F (150 ˚C) (this was possibly owing to the presence of a long side chain of poly-acrylic acid in CP2). The salt tolerance and fluid loss control performance of the polymers were better than starch.

Crosslinked AA-AMPS polymer

Gang *et al.* (2020) synthesized a deformable plugging polymer (DPP) by crosslinking AA and AMPS with MBA crosslinker. DPP showed a strong water swelling capacity and pressure sealing ability up to a temperature of 302 ◦ F (160 ˚C). The DPP was applied to 8 wells of a gas field in China to demonstrate the ability of DPP to plug the leaking formation.

Crosslinked AM-MBA microgel

Wang *et al.* (2020) synthesized a cross-linked microgel (CMG) polymer of monomer AM and crosslinker MBA using dispersion polymerization. The results indicated that the CMG polymer showed excellent thermal stability (up to 392 ◦F; 200 ˚C)). Transmission electron microscope images of the CMG polymer show spherical and oval shapes around a micron in length. The influence of initiator concentration and crosslinking agent on particle size was evaluated. The results revealed that the size of CMG polymer increases with an increase in initiator loading, whereas the size decreases with increase in crosslinking agent concentration.

Graft copolymers of natural materials

Sulfonated lignite and its derivates

Lignite is a low value coal. It is typically utilized as a thinner, filtration loss control agent, emulsifier, and rheology stabilizer in oil and gas well drilling (Fink, 2012). The stabilizing behaviour of lignite is attributed to the presence of humic acids and the associated carboxylic groups (Gavrilof and Koledin, 1999). It is believed that the hydrophilic carboxylic acid and phenolic groups in humic acid bind with clay platelets to keep the clays deflocculated and inhibit thermal-gelation of the fluid. Additionally, humic acid forms complexes with ions such as Mg^{2+}, $Ca^{2+,}$ and Fe^{3+}, therefore offering salt resistance. The phenol ring-based moieties stabilise the polymer chains, and the inflexible ring structure enhances the thermal stability of the polymer. However, lignite-based fluids are susceptible to contamination from calcium compounds and from other common salts (Monroe, 1962). In addition, these fluids require a high alkalinity during formulation and application (Monroe, 1964). These shortcomings were addressed by the development of chemically crosslinked sulfomethylated lignite polymer (Dorman, 1991). The polymer was laboratory tested and was found to provide rheological and filtration control up to 437 ◦ F (225 ˚C)). A field gypsum-based fluid was treated with modified lignite and aged at 356 ◦ F (180 ˚C). The laboratory test revealed that the addition of modified lignite reduced thermal gelation and reduced filtration loss.

Shen and Zhang (2018) reported the synthesis of lignite graft sulfomethyl phenol aldehyde polymer by polycondensation using formaldehyde and phenol. The effect of the polymer on the rheological and filtration properties of a bentonite slurry were evaluated. The polymer was found to effectively reduce the fluid loss at temperature up to 392 ◦ F (200 ˚C) and also regulated the rheological properties of the drilling fluid. The synthesized lignite-based graft polymer was a more effective fluid loss control agent than the commonly used causticized lignite additive.

Polyanionic cellulose graft AM-AMPS-SSS (PAC-g-AAS)

Poly anionic cellulose (PAC) has a molecular carboxymethyl unit (i.e., –CH2COO–Na^{+}). As the primary hydroxyl group is more reactive than the secondary hydroxyl group, the primary hydroxyl group is generally involved in carboxy methyl substitution. The functional groups associated with PAC are carboxyl and hydroxyl. As indicated, a carboxyl group is responsible for the salt (e.g., calcium and magnesium) and acid resistance of the polymer (i.e., there is no precipitation of PAC under salt contamination and acidic pH). In addition, the carboxyl group has a strong binding capacity with water and assists in forming a gel. Hydroxyl groups (secondary) have a strong water sorption capacity and form hydrogen bonds with the neighbouring glucose unit.

Owing to the presence of a hydrophobic polysaccharide backbone and many pendant hydrophilic carboxyl groups, PAC exhibits amphiphilic behaviour. PAC also displays exceptional filtration and rheological control behaviour under wide temperature variations. However, PAC cannot be used beyond 392 ◦F (225 ˚C) because of biodegradable cellulose units in the molecule.

Gautam and Guria (2020a) synthesised a PAC graft AM, AMPS, and SSS copolymer using free radical polymerization. In the PAC grafted AM-AMPS-SSS polymer, individual monomers have a specific role in improving the property of the drilling fluid under high temperature, saline, and acidic conditions. Therefore, an optimal combination of the functional groups from the AM, AMPS, and SSS monomers, should result in an excellent HT drilling fluid. The PAC grafted copolymer was used to prepare HPHT drilling fluids containing bentonite and functionalized fly ash (Gautam et al., 2018). The resulting fluid had enhanced rheology control, filtration characteristics, and lubricity at temperatures up to 437 ◦F (225 ˚C). Furthermore, the fluid remained stable (with adequate rheology, fluid loss, and lubrication properties) in solutions of NaCl (4.6 wt%) and $CaCl_2$ (4.4 wt%), and under acid contamination (pH: 6.5).

Environmental aspects

The selection of a drilling fluid generally depends on the downhole conditions of the well being drilled, its geographical location, and the prevailing environmental legislation. The oil and gas drilling industry has shifted towards low toxicity and readily biodegradable synthetic and water-based fluids to minimize the environmental effects (Fadairo et al., 2012). However, several other synthetic constituents are required to achieve high-temperature stability, desired rheological, and filtration properties at elevated temperature conditions. These synthetic additives can be toxic and pose severe threats to planktonic and marine organisms if disposed of untreated and may also enter humans through the food cycle (Balgobin et al., 2012; Landrigan et al., 2020; Pereira et al 2022).

The influence of the monomers used in the synthesis of polymers on the environment and ecosystems, including human health, are of particular concern. For example, NVP monomer is categorized in the highest hazard class, whereas AMPS is categorized in the lowest hazard class (Lithner et al, 2011; Belgacem and Gandini, 2008). When developing new polymers, it is therefore important to select component monomers with the lowest possible toxicity.

Solid Fluid Modifiers

Clay particles and modified clay particles

Laponite

Laponite is a synthetic hectorite clay with a disk-shaped structure. It has a diameter of 25 nm and a thickness of 1 nm (Xiong et al., 2019). Laponite nanoparticles offer highly diversified mechanical, chemical and structural properties along with surface charge, morphology, and biodegradability (Das et al., 2019). Xiong et al. (2019) evaluated the thermal resistance, viscosifying behaviour, and salt tolerance capabilities of laponite. The experimental results revealed that the laponite has excellent viscosifying abilities and can function at a temperature of up to 260 ◦C. The viscosifying effect of laponite was compared with commercial viscosifier HE300 and DRISCAL–D, and it was found that laponite performed better at retaining viscosity at high temperatures.

Laponite graft AM-AMPS-DMDAAC

Huang *et al.* (2019a) studied the effect of laponite nanoparticles on the thermal stability of a synthetic polymer-based fluid. First, a terpolymer (AAD) of AM, AMPS, and DMDAAC was synthesized through radical polymerization. Then laponite nanoparticles were added to formulated AAD based fluid. The experimental results suggested that laponite was beneficial in maintaining a higher viscosity and slowing down the degradation of the AAD terpolymer owing to strong electrostatic interactions and hydrogen bonding between laponite and functional groups of AAD. The formulated nano-laponite and synthetic polymer-based fluid were found to impart stable rheology up to 410 ◦ F (210 C˚).

Laponite graft AM-AMPS-DMDAAC-S

Shen *et al.* (2020) synthesized a hydrophobic associated polymer (AADS–LP) based laponite composite by in situ emulsion polymerization of monomers: AM, AMPS, DMDAAC, ST, and laponite. Morphological analysis using SEM, revealed a bean pod-like structure which was beneficial in filtration loss control. The addition of AADS–LP in freshwater-based fluid improved rheology, salt tolerance, and filtration properties under high-temperature conditions (302 ◦ F; 160 ˚C)). The polymer (AADS–LP) is absorbed on to the clay surfaces (by a combination of electrostatics and hydrogen bonding) which hydrates the clay surface preventing aggregation of the clay particles at high salinities. The improvement in filtration properties was attributed to blocking pores and cracks and forming a smooth layer of clay at the surface.

Laponite graft AM-AMPS-DMDAAC-ACMO

Yang et al. (2022) synthesised a laponite grafted polymer composite consisting of AM, AMPS, DMDAAC) and 4-acryloylmorpholine (ACMO). The apparent viscosity and yield point of a water-based mud containing the polymer composite showed an upward trend with the increasing temperature; this was irreversible. It was postulated that since as the aging temperature increases, the thermal motion of water molecules increases, the hydration shell on the particle (laponite and bentonite) surface becomes thinner, and the because of the increased Brownian motion of the particles leads to more collisions to the aggregation of the bentonite and laponite particles, resulting in an increase in particle size. The rheological properties of mud decreased significantly above 248 °F (120 °C). The apparent viscosity value was only 12 mPa·s at 392 °F (200 °C), a reduction of 90%. The authors postulate that high temperature induced polymer oxidative degradation, conformational transformation, and rupturing of hydrogen bonds, occurs which weakens the network structure and reduces the viscosity of the drilling fluids.

Palygorskite (Pal)

Palygorskite is a monoclinic phyllosilicate of magnesium and aluminium. The elongated shape of the palykorskite particles helps in dispersion, salt and alkali resistance, and high-temperature stability of drillings formulated with palykorskite. Abdo and Haneef (2013) evaluated the application of palygorskite in HPHT oil and gas drilling. The Pal nanoparticles were purified, synthesized, and further functionalized to tailor their effectiveness in controlling bentonite dispersion. It was found that Pal considerably improved the thermal stability of the fluid thus reducing the need for expensive rheology modifiers.

Sepiolite

Sepiolite is a complex magnesium silicate with a fibrous texture and offers unique structural characteristics and physio-chemical properties owing to the presence of molecular-sized channels and grooves. Carney and Meyer (1976) evaluated sepiolite as an additive for HPHT well drilling. The fluid formulation showed enhanced rheological stability up to 560 ◦F (290 ˚C); however, the reported fluid loss was high (>15 ml) owing to the spherical shape of sepiolite However, adequate filtration control can be achieved with the addition of synthetic polymers and bentonite. Bannerman and Davis (1978) formulated a sepiolite-based fluid which had better rheology control than a bentonite-lignite system. However, to achieve a high yield point, prolonged shearing was required. Owing to the lack of filtration control by macro-sized sepiolite, Abdo et al. (2016), synthesized nano-sepiolite with a 30–60 nm particle size These authors evaluated the effect of nano-sepiolite on the rheological and filtration behaviour of bentonite-based fluid under HT condition. The PV and YP of the bentonite-based fluid were found to improve by the addition of sepiolite in a temperature range of 50–180 ◦C. The addition of sepiolite caused a 15% reduction in fluid loss volume.

Nanoparticles

Nanoparticles (NPs) are engineered materials with at least one dimension in the range of 1–100 nm (Cheng, 2014). The functional properties of nanoparticles are typically attributed to their size, morphology, surface characteristics, and inner structure. The enhanced physicochemical properties and colloidal stability of NPs are ascribed to the very small size and extremely high surface-to-volume ratio (Vryzas and Kelessidis, 2017). Recent studies on NPs have been demonstrated their capabilities to improve rheological properties, reduce filtration loss and friction, increase the rate of heat transfer, alleviate shale instability and inhibit gas hydrate formation (Rafati et al., 2018; Ali et al., 2020; Al-Shargabi et al., 2022; Oseh et al., 2023).

Nano-silica and associated copolymers

Silica (silicon dioxide) nanoparticles are hydrophilic in nature and possess spherical morphology, high specific surface area, high thermal and mechanical properties. Apart from this, the shape, size, surface charge, and roughness of silica nanoparticles can be tuned for specific applications (Al-Shargabi et al., 2022). In light of the comprehensive reviews by Al-Shargabi et al. (2022), and Oshe et al. (2023) we focus here only on nanoparticles demonstrated to improve the high temperature rheological behaviour of drilling fluids.

Silica graft-p-[AM-AMPS-MA-ST]

Mao *et al.* (2015) synthesized a novel hydrophobic associated polymer-based silica nanoparticle with a core-shell structure (SDFL). The 1.0 wt% SDFL based WBM exhibited stable rheology after thermal aging at 446 ◦ F (230 ˚C) for 16 h with minimal reduction on apparent viscosity and yield point. Moreover, the SDFL polymer composite exhibited excellent filtration control with API filtration loss and HPHT filtration loss of aged fluid found to be 4.8 and 18.0 ml, respectively. Further, a 93.4% reduction in friction was observed for WBMs incorporating SDFL. This was attribute to efficient plugging by micropores which form a multi-level network structure.

Silica graft-AM-AMPS

An *et al.* (2016) synthesized a nanoparticle-based fluid loss control agent by grafting a acrylamide-based copolymer (AM-AMPS) onto modified silica. The modified nano-silica was prepared by reaction of a silane coupling agent and thereafter nano-silica graft copolymer was synthesized using surface-initiated free radical polymerization of modified nano-silica, AM, and AMPS. Average particle size and thickness of copolymer were determined using TEM and AFM analysis and were found to be 20 nm and 7.42 nm, respectively. The graft copolymer provided resistance against salinity (up to salt saturation), calcium (up to 1 wt%), and high temperature rheology (up to 302 ◦ F, 160 ˚C) in the formulated drilling fluids.

Silica graft DMAM-AMPS-MTAC polymer (NS-DAD)

Sun *et al.* (2020) synthesized a salt responsive zwitterionic polymer comprising silica nanoparticles, dimethylacrylamide (DMAM), AMPS, and 2-(Methacryloyloxy)ethyl trimethylammonium chloride (MTAC). SEM images of the NS-DAD polymer revealed a well dispersed and regular NPs of size 39 nm, whereas TEM image revealed interwoven needle-like morphology indicating successful grating of polymers onto the surface of modified nano-silica. The influence of polymer on water-based fluid was evaluated by varying dosage with hot rolling at temperature 302 ◦ F (160 ˚C) for 16 h. A filtration loss volume of 5.8 ml was observed for polymer-based hot rolled fluid, which was 97.01% less than polymer-free fluid sample indicating the effectiveness of polymer to control HPHT filtration loss. The mechanism for effective filtration control was the adsorption of NS-DAD on the clay surface to form a stable spatial network structure and effectively plug the nanopore in the filter cake. Additionally, the NS-DAD was found to impart stable rheology and filtration characteristics to a saturated salt water-based fluid at 150 ◦C owing to the shielding of electrostatic interactions of the molecular chain of the polyzwitterion resulting in a change of molecular structure from a collapsed sphere to open helix.

Multiwalled carbon nanotubes (MWNCT)

Multi-wall carbon nanotubes (MWCNTs) consist of nested single-wall carbon nanotubes[1] weakly bound together by van der Waals interactions in a tree ring-like structure. Multi-wall carbon nanotubes are also sometimes used to refer to double- and triple-wall carbon nanotubes (Iijima, 1991). MWCNT exhibits remarkable tensile strength (Yu et al., 2000), thermal conductivity (Sadri et al., 2014), enhanced elastic modulus (Kumar et al., 2015), and can be easily functionalized further to enhance rheology and filtration loss control. Abduo et

[1] Single-wall carbon nanotubes are one of the allotropes of carbon, intermediate between fullerene cages and flat graphene, with diameters in the range of a nanometre. Although not made this way, single-wall carbon nanotubes can be idealized as cut-outs from a two-dimensional hexagonal lattice of carbon atoms rolled up along one of the Bravais lattice vectors of the hexagonal lattice to form a hollow cylinder.

al. (2015) reported surface functionalization of MWCNT with a hydrophilic functional group. A conventional WBM was treated with functionalized MWCNT. It was observed that the addition of functionalized MWCNT to the drilling fluid system improved the thermal stability up to 500 ◦ F (260 ˚C). Additionally, the fluid systems were found to be free from any environmentally harmful materials. Ismail et al. (2016) investigated the applicability of MWCNTs as a primary additive to control drilling fluid performance. The MWCNTs were found to act as a rheology modifier and improved rheological properties such as PV, YP, and gel strength. Later, Ismail et al. (2018) investigated the lubrication behaviour of MWCNT and reported a 38–59% reduction of torque lubricity.

Lignosulfonate (LS) and associated copolymers

The lignosulfonates are a complex mixture of polymeric compounds typically comprising an aromatic ring, hydroxyl group, and sulfonate functional group attached to the propyl side chain. The aromatic rings provide hydrophilicity and improve thermal stability. The sulfonate group imparts ionic character and offers salt tolerance. The hydroxyl group provides sites for oxidative hydrogen abstraction resulting in the formation of LS radicals which initiate graft polymerization. The primary mechanism of lignosulfonate as a rheology modifier (thinner) is to prevent the bentonite clay platelets from bonding together by satisfying the charge at the edge of the clay plate and, therefore, eliminating the attractive electrostatic attraction between the clay particles. Despite being widely adopted, it has several technical limitations. These are: thermal degradation at temperatures greater than 250 ◦ F (121 ˚C) (Kelly, 1965), induced corrosion arising from lignosulfonate decomposed residue, interactions which reduce the effectiveness of other additives at temperature over 400 ◦ F (204 ˚C) (Meister et al., 1985). Chang et al. (2019) synthesized a novel filtration loss reducer by grafting AM and AMPS on to nano-lignosulfonate (LS). The incorporation of the amide group in the polymer backbone allows the graft polymer to absorb onto clay particles. In addition, the sulfonic acid group in the AMPS monomer attracts electrons from the –OH because of to the S – O –π bonds producing conjugation, thereby improving the ability to resist high salinities and high calcium concentration. The filtration behaviour of the graft polymer was evaluated by hot rolling a WBM at 392 ◦ F (200 ˚C) for 16 h. It was observed that the graft-LS containing drilling fluid showed a significant reduction in filtration loss volume (7.5 ml).

Discussion

ROP

Our analysis of the literature on ROP clearly shows that the key to increasing ROP is to decrease the viscosity and the density of the drilling fluid with the caveat that good hole cleaning must be maintained. For this a low density thermally stable shear thinning fluid is required.

Literature research reveals that the most successful method of reducing mud viscosity and density is to use a foamed fluid (Quintero, 2002; Al-Darweesh, 2022). These fluids also offer strong shear thinning behaviour. However, the use of foams is operationally complex and the foams themselves have limited stability especially at higher temperatures (Harris and

Reidenbach, 1987; Negrao, 1999; Li et al, 2014; Saxema *et al*, 2014; Verma et al, 2017). A promising alternative technology is the use of colloidal gas aphron (CGA) (Molaei and Waters, 2015; Alizadeh and Khamehchi, 2019; Padasar et al, 2020). CGAs are essentially *stabilised* microfoams (Save and Pangarkar 1994). Aphron-based drilling fluids have been successfully deployed in several field operations (Belkin et al, 2005). For example, CGA drilling fluids have been shown to offer an effective solution to lost circulation problems in multiple oilfield applications, particularly when underbalanced drilling is preferred. For example, it is reported that CGA based drilling fluids were successfully employed in mature low-pressure reservoirs of Lake Maracaibo. Over 90% of fluid recovery and excellent hole cleaning properties were reported (Ramirez *et al*., 2002; Montilva *et al*., 2002). CGAs in combination with calcium carbonate were used with similar success in depleted North Sea formations, where the fluid was used to seal the existing perforations during the first phase of the project (White *et al*., 2003). The authors also emphasised the attractiveness of CGA fluids in that they do not require compressors, high-pressure hoses or any other high-cost equipment required for air or foam drilling.

CGA fluids consist of many colloidally dispersed stable microbubbles most of which have a particle size of 10-100 µm, with the bigger ones reaching 200 µm. The aphron bubbles consist of a spherical core of air and a protective multilayer film. High stability, elasticity and good strength of the film enables aphrons to form a stable drilling fluid (Belkin et al, 2005). Furthermore, CGAs show favourable rheological properties. They have high viscosity at low shear rates allowing for efficient hole cleaning and carrying of the cuttings, whilst they are highly shear thinning (Khamehchi et al., 2016; Bjorndalen et al., 2008).

Three main components are required for CGA production – water, viscosifier and foaming agent (surfactant). Xanthan gum has been the polymer of choice for most CGA applications because of its high availability and low cost. However, as discussed above xanthan gum is thermally unstable for temperatures above 130 ˚C, so developing high temperature stable of CGAs is a current focus area (for example, Zhu et al, 2021). Improved thermal stability can be achieved by using polymers that have a high thermal stability and/or through the use of solid stabilisers and viscosifiers. Indeed, solids can replace surfactants in stabilising foams and CGAs (Yang et a.l, 2019) should molecular surfactants prove to be insufficiently thermally stable as well.

Polymers

Biopolymers

It is clear that unmodified biopolymers have an intrinsic thermal stability limit introduced by the presence of the acetal group in the molecule's backbone. For the unprotected acetal group, present in most biopolymers, this limit is of the order of 90 ˚C. Natural modifications of the molecule which provides some protection of the acetal groups, as present in scleroglucan, can increase the thermal stability of the molecule, although not dramatically so, achieving a stability of ca. 135 ˚C in the case of scleroglucan. Functionalisation of the biopolymers and the formation of composite with minerals and inorganic materials can raise the thermal stability of the polymer. However, this can be both expensive and difficult to achieve. Such materials do not appear to be commercially available and moreover, the benefits in thermal stability are unclear – they have not been tested at temperatures relevant to geothermal drilling.

Synthetic polymers

The data collated above has been plotted as a bar chart of maximum tested temperature at which the formulated drilling fluid exhibits thermal stability (note that the tests used, and success criteria vary with each study) against the polymer class employed (Figure 4).

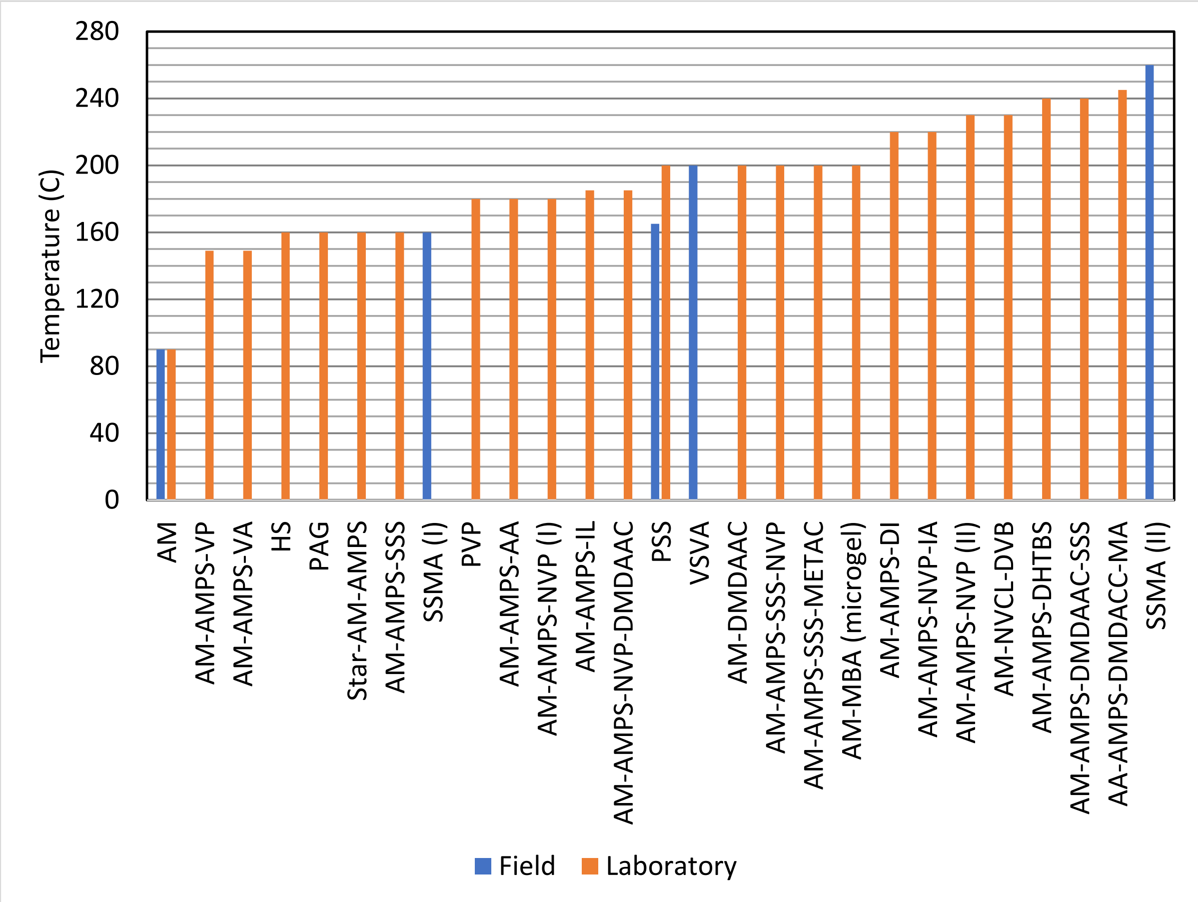


Figure 4. Thermal stability of different classes of polymer identified in the literature (field and laboratory measurements). See Table 1 for the definition of the monomers displayed. Excludes Thermal Gravimetric Analysis data.

From Figure 3 it is clear that very few of the synthetic polymers suggested for drilling fluid formulations have actually been tested in the field, the vast majority of studies being laboratory studies. Moreover, the laboratory studies do not usually cover all of the properties and duties of drilling fluids so provide a limited picture of thermal stability. Nevertheless, it is clear that synthetic polymers can offer thermal stability advantages over biopolymers although the base polymer (polyacrylamide) that forms the backbone of most water-soluble polymers also has a relatively low thermal stability, again of the order of 90 ˚C (although there is some laboratory data claiming stability up to 150 ˚C). The data clearly shows that in order to be stable at geothermal drilling temperatures, polyacrylamide must be co-polymerised with other monomers that protect the backbone. An alternative to this is make polymers that do not include acrylamide monomers. However, both solutions introduce increased cost in manufacturing the polymer (the more co-monomers there are, the higher the cost). This is clearly shown by the data supplied in Davoodi et al (2023a, 2023b) where only sodium styrene sulfonate has a lower unit cost than acrylamide (AM) and diallyl dimethyl ammonium chloride DMDAAC) is some 25-35 times more expensive than acrylamide. The most commonly employed co-monomer, 2-acrylamido-2-methy-l-propanesulfonic acid (AMPS), is ca. twice as expensive as acrylamide.

It is also clear from Figure 1 that the maximum thermal stability that has been achieved is ~260 ˚C, which whilst a considerable improvement over biopolymer-based fluids, still leaves a large window of geothermal drilling operations inaccessible to polymer-based fluids. Given the wide range of monomers employed in making the disclosed polymers and the complex molecular architectures employed, it is unclear at present how this maximum temperature can be exceeded. Given that two different versions of the same polymer (e.g., SSMA and AM-AMPS-NVP) can have dramatically different thermal stabilities, the ratio of monomers in the polymer backbone, the functional group proximity, and the blockiness of the polymer (e.g. AABBCC versus AAABBBCCC, ABCABC or ACCABB etc) must play an important part in the thermal stability. We are not aware of a systematic study of this for a given polymer type. The desired physical properties of hydrolytically thermally stable polymers should be amenable to study by computational chemistry (both atomistic and coarser grained simulations could shed light on the structure-function relationship) which, if combined with a systematic synthetic programme and simplified high throughput testing, could allow the development of novel high stability polymers. In addition, a systematic data set would be amenable to study using the machine learning methods outlined by Davoodi et al. (2023c) allowing a predictive model for the rheological properties of different polymer architecture to be predicted.

Finally, it is unclear how many of the advanced polymers are available commercially in the quantities needed for drilling, especially given the potential high cost of these materials.

As with biopolymers, thermal stability can be increased by forming a polymer-inorganic solid composite. Whilst clay-based composites use relatively cheap materials, other more complex composites do not. Currently these materials do not appear to be commercially available.

Solids

The use of solids to improve the rheological properties of drilling fluids and to improve fluid loss behaviour is an attractive option. Indeed, thermal stabilities exceeding the best synthetic polymers can be achieved (290 ˚C). Relatively cheap clay minerals and inorganic solids can offer advantages over polymers. Even simple nanoparticles can improve drilling fluid performance and thermal stability whilst having the advantage of being commercially available in large quantities.

Conclusions

1. Current key parameters governing RoP are still considered to be the 8 parameters used in the Bourgoyne-Young regression model.
    a. Many ML models based on the B&Y model have recently emerged for RoP prediction, but they do not include detailed drilling fluid properties – non-Newtonian rheology at HT, filtration (filtercake thickness / permeability), formation damage, etc.
2. RoP depends on the rheology / composition of the drilling fluid.
3. RoP increases linearly with decreasing PV, solid content, and mud weight for both sedimentary and geothermal rock formations.
4. Biopolymers are not suitable for high temperature geothermal drilling (> 130˚C)
5. Modified biopolymers and biopolymer composites may be effective above the stability limit for biopolymers alone; however, the cost of these systems will be higher and are not currently readily available.
6. Simple polyacrylamide-based drilling fluids are not recommended for high temperature geothermal operations. Modified and alternative synthetic polymers can have high thermal stability and have been demonstrated to withstand the temperatures encountered in part of the geothermal drilling window. However, the cost of these materials will be high and commercial availability is uncertain.
7. Synthetic polymer-inorganic material composites have been shown to improve synthetic polymers thermal stability. However, the limits on this are not known. Such materials are not currently commercially available.
8. Solid additives offer the potential to improve drilling fluid properties under geothermal drilling conditions. Furthermore, relatively cheap materials such as sepiolite and palygorskite can be employed. Nanoparticles offer an intriguing opportunity to modify and control drilling fluid behaviour at high temperatures using commercially available materials.

Recommendations

1. The use of biopolymers in high temperature geothermal drilling operations is not recommended.
2. Low-PV, low-solid content, and low-mud-weight drilling fluid formulations need to be developed to enhance RoP. The literature suggests that potential solutions include:
    i. Foams
    ii. Aphrons

These systems should employ HT stable polymers, particle-stabilisation, and particle composites (nanocomposites).

3. Solid additives to improve drilling fluid properties under HT geothermal drilling conditions should be investigated, especially to further develop low-PV fluids.

    i. It is recommended to further explore the use of solids to provide drilling fluid functionality under geothermal conditions.
    ii. Nanoparticle application in drilling fluids should be explored further.
4. A systematic study of the effect of copolymer architecture for a range of high performing monomers (AMPS, NVP etc) should be carried out to determine the controls on hydrolytic thermal stability. Both computational and experimental studies should be able to help elucidate the optimal structure-function relationships.
5. Polymer-solid composites should be investigated especially with the aim of improving upper thermal limits of geothermal drilling fluids.
6. Modified bio-polymer systems should be investigated to determine if it is feasible and cost-effective to extend organic polymer functionality to high temperatures.

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