AUTHOR: KAMINSKI, L.

TITLE: Increasing the temperature stability of environmentally friendly drilling and completion fluids based on organic brine.

YEAR: 2013

OpenAIR citation: KAMINSKI, L. 2013. Increasing the temperature stability of environmentally friendly drilling and completion fluids based on organic brine. Robert Gordon University, MRes thesis. Held on OpenAIR [online]. Available from: https://openair.rgu.ac.uk

This work was submitted to- and approved by Robert Gordon University in partial fulfilment of the following degree:
Master of Research, Faculty of Design and Technology, School of Engineering

School of Engineering

The project submitted in part fulfilment of the requirements for the award of:-

MASTERS BY RESEARCH (MRes) Engineering

INCREASING THE TEMPERATURE STABILITY OF ENVIRONMENTALLY FRIENDLY DRILLING AND COMPLETION FLUIDS BASED ON ORGANIC BRINE

Lauren Kaminski (1118735)

Turnitin No:26019847, Submitted on 30th October 2013

Supervisors:

Prof. Pat Pollard, Robert Gordon University

Dr. Siv Howard, Cabot Specialty Fluids, Aberdeen

Abstract

Formates provide an already superior system, designed to complement synthetic polymers and extend their temperature capabilities as drilling fluids. However, as HPHT drilling continues to move into more harsh environments with expected bottom-hole temperatures of over 300°C; further research is required to improve the temperature ceiling of eco-friendly formate drilling fluids.

The overall aim of the project was to develop a well construction fluid capable of withstanding ultra and possibly extreme HPHT temperature measures. As a result of this research, a measured combination of polyglycol sacrificial agent and MagOx has been found to inhibit the degradation of xanthan gum in formate brine so it remains stable after 16 hours dynamic ageing at 200ºC without the use of any synthetic materials. However; a formate system comprised of xanthan gum and synthetic HE® polymer was proven to function incredibly well at ultra-HPHT temperatures in excess of 250ºC for >64 hours. Thus, through utilization of improved HPHT testing equipment, it is hypothesized that the formate system and HE® polymers will remain stable in extreme HPHT circumstances i.e. over **260ºC**.

Further, there has been some dissimilarity to the literature with regards to the solubility of biopolymers in formate solutions where it has been discovered that viscosity actually increases with even less water available for hydration. It was found that the highly alkaline environment and/or buffer effect was inhibiting viscous characteristics and not the extreme concentration of salts dissolved in formate solution. The present study has also confirmed that; the order of stabilizing effects of individual cations in formate solutions generally follows the Hofmeister series of cations; Li^+, Cs^+, Na^+, K^+ with the response becoming more pronounced at higher salt concentrations. Thus, increased temperature stability of polymers and other additives can easily be achieved through simple manipulation of the formate base brine. Additionally, a significant increase in xanthan T_m of **177ºC** in 2.20g/cm^3 caesium formate was measured in the current stock - 20ºC higher than original values recorded for the Formate Manual.

Declaration

I declare that the work presented in this thesis is my own, except where otherwise acknowledged and that this thesis was composed by me. All cited references are listed at the end of the thesis. No part of this thesis has been represented for any degree or qualification at any other academic institution.

……………………………….. Date

Lauren Kaminski

Acknowledgements

First of all, I am sincerely grateful for the excellent guidance and support of my industrial project supervisor and R&D Manager, Dr. Siv Howard. The generous extent of time allocated for answering my endless questions on the topic is very much appreciated and will not be forgotten. I am also grateful for the help and advice of my RGU Supervisor, Prof. Pat Pollard on university and academic specifications concerned with the research methods courses and final write-up.

Further, I would very much like to thank Bob Frost, Laboratory Manager for his immense patience and consideration during the course of the MRes project. I am extremely lucky to have worked with such great and understanding colleagues throughout this part-time course with regards to time allocated for laboratory work and thesis write up. Also, the expansive knowledge and enthusiasm shared from John Downs, CSF consultant on the project topic has been a great influence for moving forward which I have largely appreciated. I would like to thank Stuart Leon, Technical Services Engineer for his generous help and encouragement throughout. Likewise, my fellow laboratory colleagues all through the project timeline; Craig Gordon, Craig Melton, Marcin Chrenowski, Stephen Waldram, Zhao Anderson and Will Bond have always offered their support with general day to day issues and assist when laboratory testing doesn’t always go to plan, which I am deeply grateful for.

Lastly, I would like to thank my boyfriend Dan, my family and friends for their extreme tolerance and encouragement throughout the project duration.

Table of Contents

Abbreviations

AHR – After Hot-Rolling

AMPS - 2-acrylamide-2-methylpropanesulfonic acid sodium salt

A_w – Water Activity @ 25^{o}C

Ba^{2+} - Barium cation

BHR – Before Hot-Rolling

CSF – Cabot Specialty Fluids

Ca^{2+} - Calcium cation

$CaCl_2$ – Calcium Chloride

CM Guar – Carboxymethyl guar

Co^{2+} - oxidizable Cobalt

cP – centipoise

Cr^{2+} - oxidizable Chromium

Cs^{+} - Caesium cation

Cs AcFo – Caesium Acetate/Caesium Formate (50:50) blend

CsCOOH – Caesium Formate

CsFo – Caesium Formate

Cs/K – Caesium/Potassium

Cu^{2+} - oxidizable Copper

Fe^{2+} - Ferrous Iron

Fe^{3+} - Ferric Iron

Fo - Formate

g/L – grams per litre

$HCOO^{-}$ - Formate Anion

H_2O_2 – Hydrogen peroxide

HPHT – High Pressure/High Temperature

HSO_3^- - Hydrogen sulphite

K^+ - Potassium cation

KCl – Potassium Chloride

K_2CO_3 – Potassium Carbonate

KCOOH – Potassium Formate

KFo – Potassium Formate

$KHCO_3$ – Potassium Bicarbonate

KI – Potassium iodide

Li^+ - Lithium cation

LSRV – Low shear rate viscosity

LV – Low viscosity

MagOx – Magnesium oxide

MEA - Monoethanolamine

MEG – Monoethylene Glycol

Mg^{2+} - Magnesium cation

Mn^{2+} - oxidizable Manganese

Na^+ - Sodium cation

NaCl – Sodium Chloride

NaCOOH – Sodium Formate

NaFo – Sodium Formate

PAC – Poly anionic Cellulose

PEG – Polyethylene glycol

PHPA – Partially Hydrolysed Polyacrylamide

ppb – pounds per lab barrel

PV – Plastic viscosity

RGU – Robert Gordon University

rpm – Revolutions per minute

sg – Specific gravity

$T_{50\%}$ - Temperature at which 50% viscosity loss is experienced (MARS III data)

TAME – Thermally Activated Micro Emulsion

TCT – True Crystallization Temperature

T_m – Melting temperature

TM – Transition metals

UHP – Ultra high pressure

UHT – Ultra high temperature

V^{2+} - oxidizable Vanadium

XHP – Extreme high pressure

XHT – Extreme high temperature

YP – Yield Point

List of Figures

List of Tables

Chapter 1 : Introduction

Drilling industry emphasis in recent years has been largely focused on controlling the rise in drilling costs by designing fluids which reduce the time required to drill the well i.e. faster penetration and less hole-problems. However, the search for petroleum is becoming increasingly extreme in terms of depths, temperatures and pressures, and more challenging HPHT (high-pressure, high temperature) drilling operations are being explored. As a result, there has been a rise in the demand to develop fluid additives or polymers which can enhance stability of drilling fluids to perform effectively under these intense conditions. This chapter provides a general background and literature review relevant to the main project aims and objectives.

1.1 Drilling, Completion and Work over Fluids

1.1.1 Properties of Drilling Fluids

A drilling fluid (sometimes referred to as a drilling mud) is a circulating fluid composed of a complex blend of materials, used in rotary drilling. It is designed to perform any or all of the various functions required to enable successful completion of a drilling operation (Fink 2011).

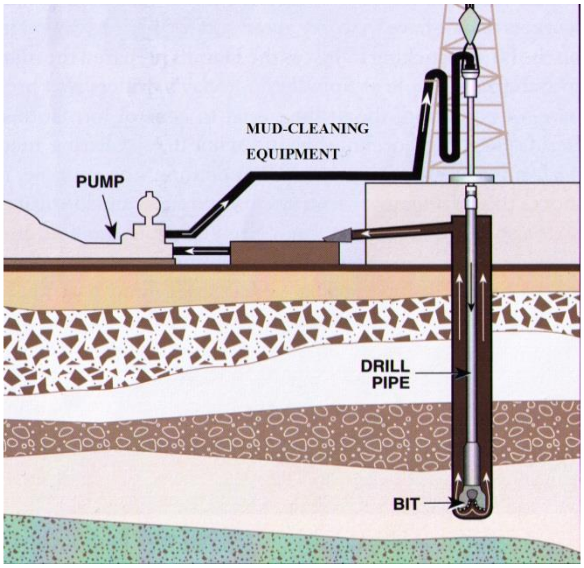


Figure 1.1 *Drilling Fluid Circulation System (Adapted from Baker 2001)*

During the circulation process (**Figure 1.1**); the drilling fluid is pumped down the drill string and sheared through the drill bit, which then flows back up the annulus to transport cuttings from the borehole to the surface for disposal (Baker 2001). However, since the oil industry has advanced to drilling in more adverse environments, it is essential that drilling mud's are continuously improved in order to satisfy the various operational demands and challenges that occur in problematic subterranean wells (Caenn, Darley and Gray 2011).

In addition to cuttings removal, several other basic functions are required of today's drilling fluids, such as (Apaleke, Al-Majed and Hossain 2012; Fink 2011);

- Cool, clean and lubricate the bit,
- reduce friction between the drill string and the side of the hole,
- control subsurface formation pressures,
- overcome the fluid pressure of the formation,
- suspend cuttings if drilling is discontinued,
- wall the hole with a thin, low permeability filter cake,
- inhibit reactions with water-sensitive shale and
- avoid damaging the producing formation.

These fundamental properties are either obtained from specialized additional products, or inherited naturally from the continuous phase or base fluid.

1.1.2 Types of Drilling Fluids

In rotary drilling, drilling muds are classified according to the primary base fluid used in their preparation. Traditionally, these are either water, oil, or gas-based, which are applied dependent on individual well characteristics, down-hole properties and cost considerations. Gas-based drilling mud's are cheap and readily available, but are often not used in oil and gas applications as they are unsuitable for drilling through water bearing zones. Water based muds in general, are still the most commonly used fluid type worldwide; however certain limitations render them inadequate for the more advanced drilling applications. Moreover, oil-invert emulsion based fluids are widely known in industry to be the most stable and effective when drilling in areas where the formation is water-sensitive and an extremely high geothermal gradient can cause concern. However, due to the increasing awareness and pressure from environmental agencies, as well as high costs of cuttings and fluid disposal, water-based mud’s which simulate the performance of oil-based drilling fluids, are rapidly becoming more popular – for example, formate-based fluids (Apaleke, Al-Majed and Hossain 2012).

In addition, a relatively new generation of drilling muds based on synthetic fluids (e.g. esters, ethers, and polyolefins) have been designed to employ the advantages of oil-based muds, without the stringent environmental restrictions and cost involved with their disposal (Caenn and Chillingar 1996). Still, drilling waste associated with synthetic based muds is considerably less dispersible than water-based fluids, as their counterparts can often sink to the seafloor and cause potential environmental concern towards aquatic life (Sadiq et al. 2003).

Table 1.1 General Advantages and Disadvantages of Drilling Mud Classifications

Properties	**Mud Classification**			
	Water-Based Mud	**Formate-Based Mud**	**Oil-Based Mud**	**Synthetic-Based Mud**
Thermal Stability	✗	✓	✓✓	✓✓
Shale Inhibition	✗	✓✓	✓✓	✓✓
Low Solids Loading	✗	✓✓	✗	✗
High ROP	✗	✓✓	✓	✓
Lubricity	✗	✓✓	✓✓	✓✓
Fluid Loss Control	✗	✓	✓✓	✓✓
Bacterial Control	✗	✓	✓✓	✓✓
Low Toxicity	✓✓	✓✓	✗	✓
Cost	✓✓	✗	✓	✗
Environmental	✓✓	✓✓	✗	✓
Low Corrosivity	✗	✓	✓	✓

KEY: Very Good ✓✓ Good ✓ Bad ✗

Table 1.1 characterizes the different base mud types and their general superiority ratings with regards to individual fluid properties. Advantages and disadvantages of each are heavily evaluated with regards to the mud selection process for specific well considerations.

1.1.3 Reservoir Drilling Fluids

In recent years, advanced drilling technologies such as high-angle, multilateral, slim-hole, high-pressure, high temperature (HPHT), deep discovery wells have led to the development of a special class of maximum performance drilling fluids, more commonly referred to as reservoir drilling fluids (RDF's) or "drill-in" fluids. These are essentially completion fluids, which possess the multi-functional requirements of a drilling fluid in addition to the non-damaging behavioural characteristics of a low-solids brine or oil-fluid. In the field, engineers replace the conventional drilling fluid with a "drill-in" fluid of a similar base just before the pay zone has been reached, then if applicable it can be utilized until the end of the completion operation (Fink 2011; Ezell et al. 2010).

RDF's are designed primarily to optimize wellbore productivity by preventing formation damage in the producing interval. Other important characteristics required of RDF's include; superior hole cleaning, increased rate of penetration (ROP), with low equivalent circulating densities (ECD's), reduced sag of weighting material, and a decreased wellbore clean-up effort. High ECD's are typical of high density solids loading in conventional mud's which in turn can increase the risk of fracturing the formation making it necessary to reduce circulation rates, thus reducing ROP and compromising hole cleaning, providing a negative "knock-on effect" (Ezell et al. 2010; Berg et al. 2007). A "drill-in" fluid that can maintain effective suspension properties over a broad spectrum of conditions is representative of a good RDF which in turn, will promote favourable hole-cleaning and alleviate sag issues. These exceptional fluids are always formulated to enhance low shear rate viscosities, effectively lowering ECD's and minimizing rig time by allowing drilling to proceed at a faster rate (higher ROP).

Solids such as calcium carbonate or sized salts are selected to provide some density and fluid loss control in most "drill-in" fluids, as they are acid-soluble and therefore, easily removable for an effortless clean-up. However, the ultimate objective is to provide density without the use of excess weighting agents (which can result in undesirable high plastic viscosities and clean-up difficulties); this can be achieved by the utilization of high density brine systems (Caenn, Darley and Gray 2011; Ezell et al. 2010).

Although water and oil-phase fluid RDF systems still exist, most of those which are utilized in recent field operations have been brine based "drill-in" fluids (Ezell et al. 2010). Therefore, the development of an improved performance brine-based system which can function effectively in extreme thermal and pressure conditions while drilling complex formations is of industry wide interest.

1.1.4 Completion and Work over Fluids

After the drilling phase of a well is complete, the drilling mud will be replaced by a clean non-damaging fluid for completion and work over operations. Completion fluids are used to facilitate final operations prior to the initiation of production such as setting production liners, packers, down-hole valves or perforating into the producing zone. They are usually solids-free, low-solids brine or oil-based fluids designed to exert minimal impairment on the productive formation or reservoir. Solids-laden fluids are generally undesirable in this respect as they can block equipment, preventing tools from being set correctly, and cause plugging of perforations and gravel packs ultimately leading to an overall reduction in productivity. Non-aqueous oil or synthetic based fluids are also used in completion, but require a more complicated clean-up process where a sequence of surfactant pills have to be circulated to remove mud residue from the wellbore and casing (Caenn, Darley and Gray 2011; Moroni, Fraser, et al. 2008).

The term "work over" is used to describe a process involving the repair or stimulation of a well to enhance productivity if the original hydrocarbon yield after completion is lower than expected. Therefore, a work over fluid is required to provide hydrostatic well control and often fluid loss properties during intervention procedures (Gonzales, Quintavalla, et al. 2013). Their characteristics are generally similar to those of completion fluids and it is customary for the same fluid to be re-used in both operations.

1.1.5 HPHT Wells and Drilling Fluids

The continuing growth in the industrial demand for energy has led to oil and gas reserves being sought after in increasingly more extreme environments with regards to greater depths, pressures and temperatures. Thus, the requirement for innovative new fluid technologies is of utmost industry interest for the future of high pressure/high temperature oil and gas drilling and completion applications. The most common definition of a standard HPHT condition is; a well accompanying temperatures and pressures which are likely to exceed 150ºC and 10,000psi respectively (or with a pore pressure higher than 0.8 psi/ft.).

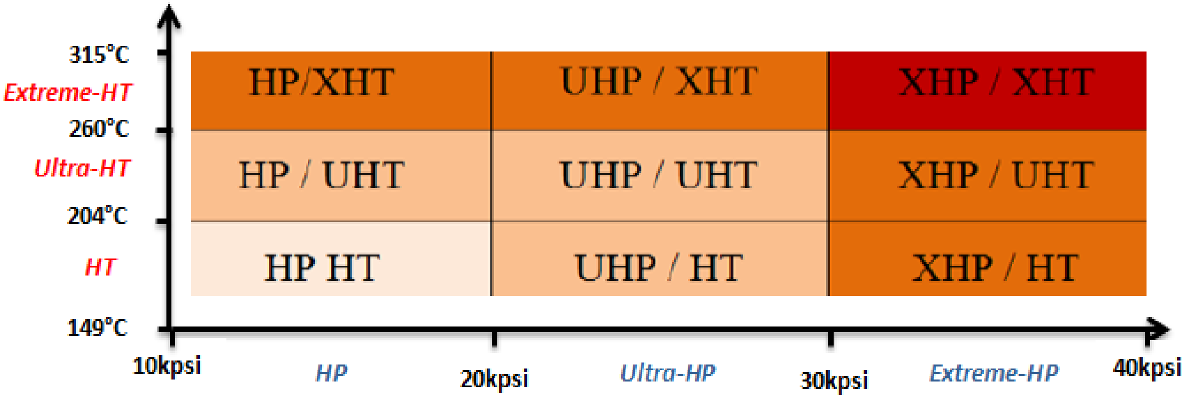


Figure 1.2 *Matrix of High Pressure/High Temperature operation (Adapted from (Shadravan and Amani 2012)*

Generally speaking, there are three categories of HPHT drilling; standard HPHT, ultra-HPHT and extreme HPHT and their conditions are all depicted in **Figure 1.2**. Different service companies, operators etc. have their own definitions for HPHT classification; most of which are very similar, however ultra and extreme HPHT are reversed in some cases depending on the corporation (see **Table 1.2**). With regards to the current study; for improved consistency, reference to **Figure 1.2** will be employed for all further HPHT stipulations (Shadravan and Amani 2012; Madu and Akinfolarin 2013).

Table 1.2 Varied starting temperatures and/or pressures for HPHT, ultra-HPHT and extreme-HPHT conditions from the different oil service companies (Adapted from (Shadravan and Amani 2012)

Company	**Baker Hughes**		**Schlumberger**		**Halliburton**	
	Pressure (psi)	**Temp (ºC)**	**Pressure (psi)**	**Temp (ºC)**	**Pressure (psi)**	**Temp (ºC)**
Standard HPHT	15,000	177	10,000	150	10,000	150
Ultra-HPHT	20,000	204	20,000	205	20,000	200
Extreme-HPHT	30,000	260	35,000	260	15,000	175

Due to the relatively short history of HPHT advances, the additional challenges in which modern drilling fluids need to contend with compared to conventional practices are;

- **Increased mud weights:** The mud weight requirement is normally much higher for HPHT drilling as formation pressures increase progressively the deeper the distance drilled so the equivalent density is needed for well control purposes. Issues with barite sag and gelation are incessant obstacles for HPHT drilling fluids with regards to high frictional losses during circulation and unacceptable ECD’s, so the utilization of high density base fluids is recommended to reduce solids loading. Further, mud weight must be closely monitored due to narrow operating windows between the formation pressures and corresponding fracture tension (Godwin Jr., Ogbonna and Boniface 2011).
- **Low ROP in the producing zone:** Due to highly compacted formation geometries at HPHT depths, ROP is much slower and in some cases is being reported as only 10% of the speed of ordinary drilling conditions (Shadravan and Amani 2012). Thus, the HPHT fluid should be engineered towards minimizing any further decrease in ROP i.e. lower viscosity.

- **Corrosion:** An influx of acid gases, either carbon dioxide (CO_2) and/or hydrogen sulfide (H_2S) from the reservoir are the most probable causes of corrosion in HPHT circumstances. Since corrosivity is determined in part by pH; the rates of general and pitting corrosion are substantially increased in fluids not protected by an alkaline buffer system (Howard and Downs 2009).
- **Polymer degradation at HPHT:** In conventional water-based drilling fluids, common biopolymers tend to degrade quickly in HPHT environments causing the suspension and fluid loss attributes to fail. For this reason, synthetic polymers are selected for use at higher temperatures - but they normally lack the shear thinning characteristics of natural polymers so rheological properties become less ideal. Additionally, even with the utilization of novel synthetic materials, at some point they are likely to also degrade especially in ultra and extreme HPHT territories.

For this reason, advances in mud design are of key importance as the future of oil well drilling is progressively moving into deeper wells with even higher temperatures and pressures so the current categories of HPHT will only increase further in coming years.

1.2 Applications of Formate Brines in the Drilling Industry

1.2.1 Formate Brines as Drilling, Completion and Work over Fluids

Formate brines are the aqueous solutions of alkali metal salts of formic acid. They are monovalent, low-solids, high density, environmentally safe clear fluids which exhibit non-damaging behaviour in the reservoir (Howard 2011a). **Figure 1.3** illustrates the three formates considered most useful to the oil industry by order of increasing density and solubility; sodium, potassium and caesium formate. They are extremely soluble in water to provide an ideal base for any reservoir drilling or completion fluid, without the added controversy of stringent environmental regulations customary to oil-muds. Formate brines have a proven track record of enhancing productivity in challenging operational environments. In fact, Howard and Downs 2005, stipulated that in nearly all reported field cases of formate use in drilling and completion, the well production rates have been significantly higher than expected (Byrne, Patey, et al. 2002; Howard and Downs 2005). This contribution along with many other favourable characteristics makes these brines, especially valuable in their applications to the drilling industry today.

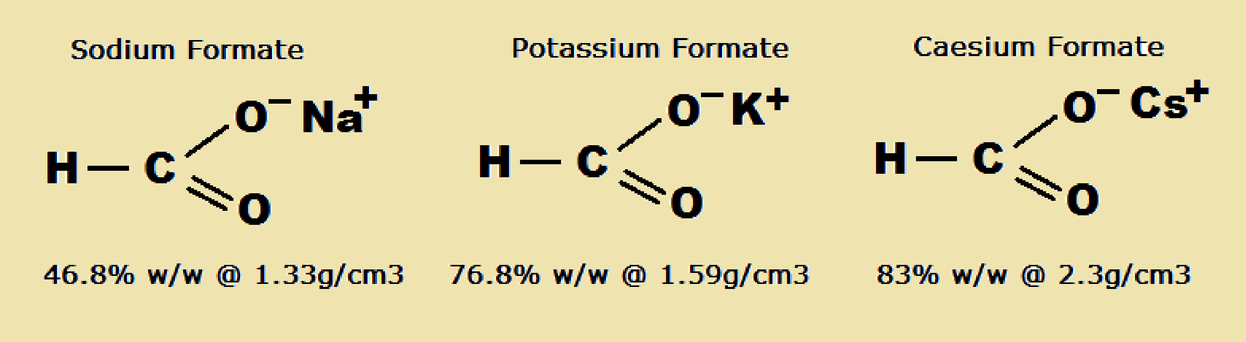


Figure 1.3 *The chemical structures of the three formates in order of increasing percentage weight solubility in water (Adapted from Howard 2011a)*

The increased hydrocarbon productivity observed after using these brines for drilling and completion has been well documented in literature, and illustrate they are highly compatibility with reservoir fluids and minerals under realistic reservoir conditions. The formates were originally introduced to the field in 1993 after completing a coiled-tubing job in The Netherlands in the form of sodium formate brine. Less than a year later, potassium formate was selected for use in a reservoir “drill-in” operation in Norway with promising results, yet it wasn’t until 1998 that extremely high density (up to 2.30g/cm^3) caesium formate brine became commercially available for drilling and completion purposes (Byrne, Patey, et al. 2002).

Caesium, potassium and sodium formate fluids cover the whole density range typically required in drilling and completion. Being free of excess solids such as barite, high-density clear brine systems, in general will exhibit lower plastic viscosities, and therefore lower ECD’s. Formate brines offer a viable option for reducing the problems encountered by high solids loading. Their “flat-rheology” among many other idealistic properties demonstrate that formate drilling mud’s make excellent RDF's. In an experimental study, Ramsey, 1996 reported dramatic increases in drilling rates (ROP) using caesium formate mud compared with a water-based haematite mud weighted up to the same density – in nearly every case, the improvement was 100% or more. The control measure was prepared using haematite as the weighting agent instead of barite as it has a higher specific gravity and therefore lower solids would be required to achieve the same density. The author had fully anticipated that, had a barite weighted water-based mud (WBM) been used, the caesium formate mud would have performed even better by comparison as the additional barite solids would have slowed ROP even further (Ramsey et al. 1996). In addition to Ramsey's study, Black *et al*, 2008 achieved 100% increased ROP in laboratory tests using a 1.90g/cm^3 caesium formate brine in comparison with the same density oil-based mud. Further analysis illustrated that a caesium formate mud (with all of its usual additives) can also increase ROP by as much as 80%. Oil-based fluids are promoted to allow faster drilling rates than conventional water-based mud's, but caesium formate acts by the mechanism of increasing both the efficacy and aggressiveness of the bit to enhance ROP further than alternative water or oil based fluids (Black et al. 2008).

Another useful characteristic of formate brines is their powerful shale inhibiting properties, which in essence, discourages them from reacting with shale or other water-sensitive formations in the well. Laboratory tests have indicated that shale integrity and strength actually increases when exposed to formate based fluids. Potassium formate is potentially the strongest inhibitor of the formate family and promotes shale drilling by reducing the swelling pressure, shale water content and pore pressure. To achieve effective shale stabilization at higher densities, potassium formate can be blended with caesium formate - the mechanism combines high filtrate viscosities with low water activity to inhibit common reactions with shale (Bungert, Maikranz, et al. 2000; Ramsey et al. 1996).

Inferior shale inhibition is a major limitation of most conventional WBM's and coincides with lost time and trouble costs for the operator. The decision to opt for less ecological but more technically stable OBM when drilling highly water-sensitive areas is usually approved. However, as an environmental alternative to oil-based mud, Hallman and Bellinger, 2003 illustrated in multiple field trials that potassium formate brine showed dramatic improvements in minimizing formation damage and shale dispersion when incorporated into a conventional WBM at fairly low concentrations (5-10%). Based on these findings, formate-based mud systems have since been endorsed to drill over 400 wells through troublesome shale's in western Canada, primarily for their exceptional inhibiting capacity (Hallman and Bellinger 2003).

Maintaining a low ECD in long/narrow boreholes and eliminating solids sag at high temperatures is a major advantage of the formate brines and is critical for well control purposes (Byrne, Patey, et al. 2002). High ECD's while circulating barite laden drilling mud's is a frequent cause of well bore fracturing in deep gas formations where a narrow operating window between the pore and fracture pressure exists. Also, common water-based system viscosifiers tend to break down at high temperatures, causing dynamic and static barite sag as well as increasing the risk of well control incidents in high angled wells. Oil-based muds are capable of absorbing large volumes of reservoir gases, so a kick cannot be easily identified, which can also lead to massive well-control issues. In addition to corrosive gases, an influx of hydrocarbon gas may destabilize an oil-based formulation and cause the fluid to sag (Downs 2010). Changes in volume and density of a drilling fluid as the result of a gas influx can have severe consequences, with regards to stability of the well. Formate brines have a low gas solvency, much lower than oil-based fluids and significantly lower than in water, thus they cannot be destabilized by the influx of hydrocarbons or corrosive reservoir gases, which allows for better kick detection and faster flow-checks in formate-based fluids (Downs 2010; Howard 2007).

There are many reasons why formate brines are considered the preferred choice for drilling and completion operations in particularly challenging subterranean environments with narrow margins between the pore pressure and fracture pressure, or tight "hydraulic operating windows." But arguably the biggest advantage of them all is their ability to increase the temperature stability of important biopolymers allowing them to function effectively at very high temperatures.

1.2.2 Formate Brines Increase the Temperature Stability of Polymers

It has been well documented in literature that the formate salts increase the stability of biopolymers to far greater temperatures than conventional oil-field brines due to their unique ability to solubilize at extremely high concentrations in water for example, up to 83% w/w in caesium formate (Messler et al. 2004; Howard 1995). Further, aside from their extreme salinity, formate brines possess numerous other properties which enable them to contribute to the polymer stabilizing effect;

- **Anti-oxidant capacity:** The formate ion is a powerful antioxidant, readily scavenging hydroxyl free radicals which can increase the hydrolytic degradation rate of water-soluble polymers and additives in solution.

- **Water-structuring effect:** The alkali metal formates exert a structuring effect on surrounding water molecules or “salting-out” effect which allows dissolved macromolecules to become more ordered, rigid and stable at high temperatures (Caenn, Darley and Gray 2011).

- **Low water activity:** The thermal stability of drilling fluids can be largely dependent on hydration reactions between polymers. Therefore, formate brines having a low water activity is beneficial as it protects water-soluble biopolymers by inhibiting microbial growth, either at the surface of the well or down-hole (Howard and Downs 2005).

- **Naturally alkaline pH:** Formate brines exhibit an alkaline pH 8-10, which helps control corrosion, lower formate decomposition rate and contribute to polymer stability at higher temperatures by preventing the pH decreasing to a range where acid hydrolysis can occur (Howard 2011a).

In order to maintain an alkaline pH in HPHT conditions, it is essential that carbonate/bicarbonate pH buffer is added to any formate-based well construction fluid. Dissolved polymers can rapidly degrade in acidic environments by acid hydrolysis, for this reason it is assumed that formate fluids can be made more thermally stable by managing the amount of carbonate/bicarbonate added to the formulation (Howard and Downs 2009).

With regards to polymers, their temperature stability can generally be enhanced by ensuring the concentration of formate salt in solution is kept as high as possible. Since potassium formate can obtain the highest molar concentration out of the three alkali metal formates, an optimized blend of potassium and caesium formate is suggested to achieve optimum stability for densities between 1.59 and 2.20g/cm^3 accordingly, and vice versa for sodium and potassium formate at the lower densities (Howard 1995).

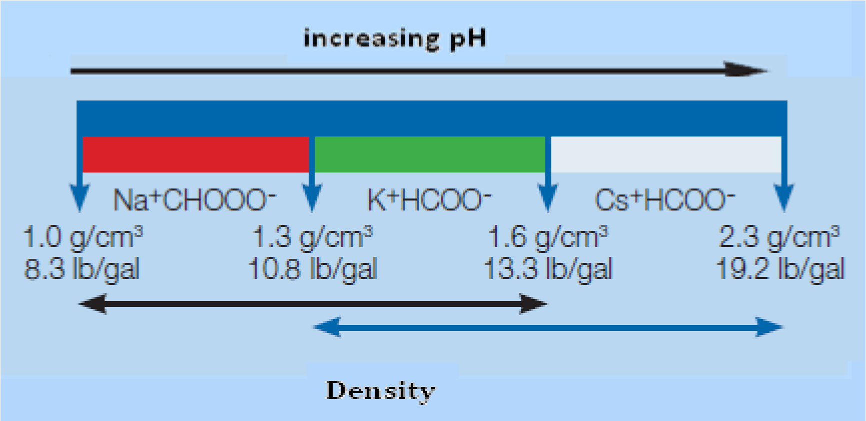


Figure 1.4 *Sodium, potassium and caesium formate in order of increasing density and pH (Adapted from Howard 2011a)*

Although it is established that polymer stability is maximized at the higher salt concentrations, some improvements in stability can be observed even with very low levels of formate additions. Oswald *et al*, 2006 acknowledged a field trial offshore in the United Arab Emirates where only 20 lb/bbl sodium formate salt was added to a sodium chloride based drilling mud to prevent polymer degradation with prolonged exposure to BHT's over 150°C. Subsequently, this small inclusion of sodium formate reduced the consumption of fluid additives by 66%. With that said, several laboratory and field cases reported have indicated that the formate base fluid needs to be at full or near saturation in order to achieve stability at temperatures over and above 160°C (Oswald, Knox and Monem 2006). For example; Messler *et al*, 2004 stipulated that most formate fluids (at saturated concentration) will stabilize biopolymers up to 175°C. However, for the mud to retain relevant properties in order to function effectively at temperatures over 200°C; additional stabilizing chemistries (anti-oxidants and thermal extenders) need to be incorporated into the fluid. Another consideration when mixing formate fluids is that it is thought that polymer hydration requires extra time and heat in saturated brine, so occasionally brine densities have been lowered slightly by addition of water in order to obtain the maximal yield of polymer (Messler et al. 2004).

1.3 Polymers for Drilling Fluids

1.3.1 Polymer Behaviour in Solution

Polymers are organic colloids composed of unit cells (monomers), linked together in straight or branched chains to form macromolecules. They can be classified as natural, modified natural or synthetic and their main function in drilling fluids is to provide viscosity and/or fluid loss control (Caenn, Darley and Gray 2011).

The behaviour of polymers in solution is dependent on a combination of specific properties; such as molecular geometry (see **Figure 1.5**) and/or electrostatic charge associated with its counter-ions. Whether the polymer is linear, branched, cross-linked or both; this can affect viscosity characteristics due to their spatial arrangements and affinity to create interactions between adjacent polymer chains.

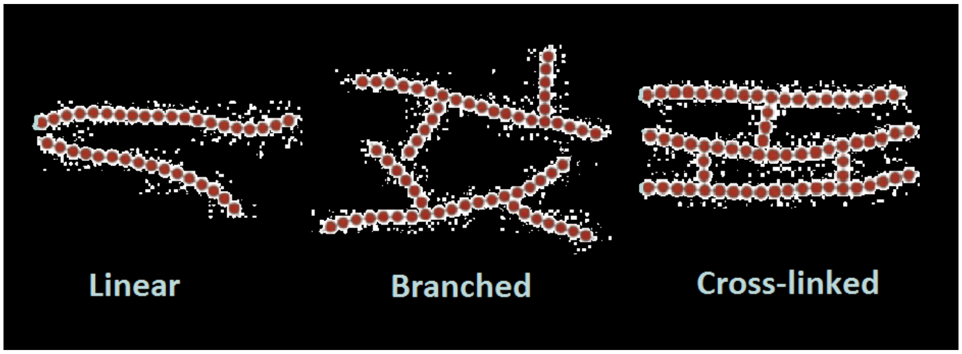


Figure 1.5 *Molecular Geometries of Polymers (Adapted from Caenn, Darley and Gray 2011)*

According to their electrostatic charge, water soluble polymers can be classified in any three basic groups; anionic, cationic and non-ionic. Most polymers commonly used in the oilfield are anionic in nature, with a negatively charged functional group (usually formed by the dissociation of an acid group). Less common are cationic polymers, most often amine-type additives, whose functional group is positively charged. Non-ionic polymers contain little or no charge and therefore do not ionize in solution (Moreno 2011).

Generally, when a single polymer molecule dissolves in a compatible solvent, it swells (or "hydrates") as the solvent penetrates the molecule and assumes a conformation determined by the stiffness of polymer backbone and its affinity for the solvent. The addition of further polymer molecules enhances their interactions decreasing the volume of space occupied by a single polymer molecule. Thus, after the critical polymer concentration, the molecules cannot contract any further and eventually strongly interpenetrate with one another – this is known as cross-linking (Lei and Clark 2004).

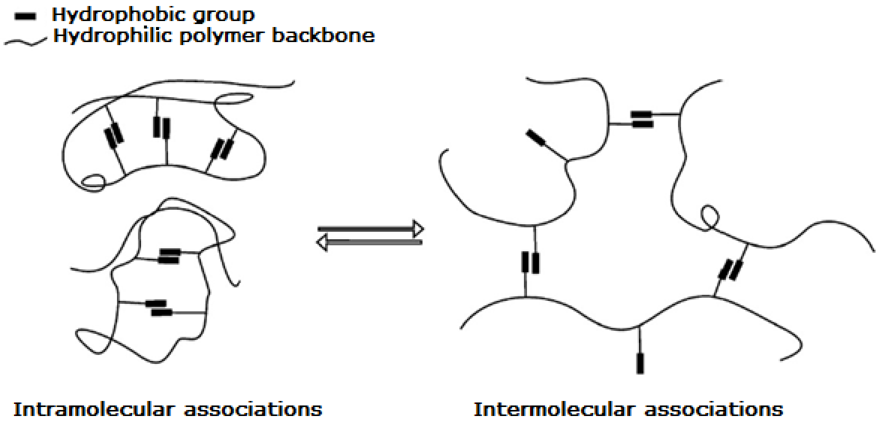


Figure 1.6 *Intra- and intermolecular cross-linking interactions (Adapted from (Wever, Picchioni and Broekhuis 2011)*

In solution, there are two types of cross-linked responses to form polymer gels; intramolecular reactions which occur within a polymer molecule, and intermolecular associations that develop between neighboring polymer chains (see **Figure 1.6**). These reactions are largely affected by the concentration of polymer and the presence of added salts in solution. The rule is; if the concentration of electrolyte is high, then the likelihood of intramolecular associations increases ten-fold due to contraction of polymer molecules by the salts "screening" effects. Hence, intermolecular interaction is more prominent in purely aqueous solution as the polymer molecule occupies a larger hydrodynamic volume (Wang, Lu, et al. 2008).

All of these properties; molecular geometry, electrostatic charge and affinity for salts widely contribute to the polymer's solution viscosity and important rheological characteristics within the field of drilling fluids.

1.3.2 Rheological Effect of Polymers in Drilling Fluids

The term "rheology" refers to the branch of physics that regulates the deformation or flow of matter. In water-based drilling fluids, specific additives or polymers are supplemented into the base brine to deliver ideal rheological properties which carry out essential functions of the drilling mud such as improved hole cleaning and solids sag prevention. Thus, the viscosity must be high enough to suspend any solids or cuttings when drilling is discontinued, but still thin enough as to promote faster drilling rates upon recirculation. Further, it is recommended to minimize cuttings bed consolidation to optimize hole cleaning as much as possible, and this can be achieved through reduced gel strengths. In essence; the less strain required to break the gel, the easier the cuttings are removed – which is endorsed by adopting polymers with pseudoplastic (or shear thinning) tendencies (Saasen and Løklingholm 2002).

If a polymer is shear thinning; at low shear rates the stretching macromolecules intertwine to form aggregates, and the highly viscous response is due to the polymers large resistance to flow. Increasing shear rate destroys aggregates and thus the fluids flow resistance declines, resulting in a decrease in apparent viscosity. Upon removal of shear, viscosity begins to increase almost instantaneously; this behaviour largely results from the ability of polymers to form rigid structures and entanglement through increased hydrogen bonding (Xu et al. 2013).

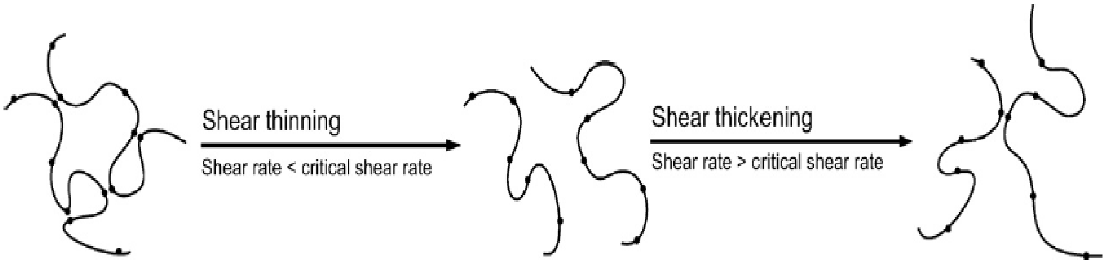


Figure 1.7 *Rheological behaviour of synthetic polymers depending on critical shear rate (Adapted from Wever, Picchioni and Broekhuis 2011)*

On the other hand, specific synthetic polymers such as partially hydrolyzed polyacrylamide (PHPA) have been shown to exhibit pseudo-dilatant (or shear thickening) properties above a given shear rate which is highly undesirable for use in a drilling fluid. Above a given shear rate; the onset of shear thickening can occur in susceptible polymer solutions due to a coil-stretched transition induced by stronger interchain synergy involving the formation of additional links between chains (see **Figure 1.7**). The critical shear rate for onset of shear thickening is dependent on the temperature and quality of solution, presence of salts, molecular weight and degree of hydrolysis of the polymer (Wever, Picchioni and Broekhuis 2011).

In the field, it is common practice for mud engineers to analyze viscosity using Bingham terminology; plastic viscosity (PV) or yield point (YP) values easily calculated from basic Fann35 rheological data. Plastic viscosity or PV is sensitive to the concentration of solids in a drilling mud, so if too high may require dilution. However, yield point (or YP) is affected largely by the electrochemical environment or inter-particle bonding and thus if not in the recommended range; demands chemical treatment to improve hole cleaning characteristics (Caenn, Darley and Gray 2011). Anionic polymers tend to decrease YP with increasing concentration, but non-ionics generally increases it so Bingham plastic rheology can also be manipulated by altering the charge density of water-soluble polymers (Tehrani 2009).

1.3.3 Biopolymers

The major advantages of biopolymers such as xanthan over synthetic polymers used in drilling and completion fluids, are they are more ecological being biodegradable, have increased resistance towards mechanical degradation and demonstrate strong shear thinning properties. Section **1.3.3** provides a general background and literature review of the relevant biopolymers and their rheological behaviour in solution.

Welan gum:

Welan gum; produced by *Alcaligenes sp.* is a useful aid for oilfield applications as it can remain stable in pure aqueous solution up to 150ºC, which is highly desirable for a natural biopolymer. Another interesting characteristic of welan gum compared to other polysaccharides is that it is soluble in polar organic solvents, such as glycols (Member and Morris 1995).

Welan gum adopts a different structure to the similar polysaccharide xanthan; in which the flow of molecules are limited due to the zipper model arrangement of double helices (see **Figure 1.8**), making it less sensitive to high temperatures and salinity. This is partially due to the positioning of acyl and glyceryl groups which increase the flexibility of molecular bundles, lowering the charge density to promote further interhelical association. The enhanced electrostatic repulsion of xanthan gum increases the difficulty of molecular aggregation, as its charge density is much higher than that of welan's. In addition, xanthan's acetyl groups are located on the side chains making it more difficult to form regular double helices due to the steric effect (Xu et al. 2013).

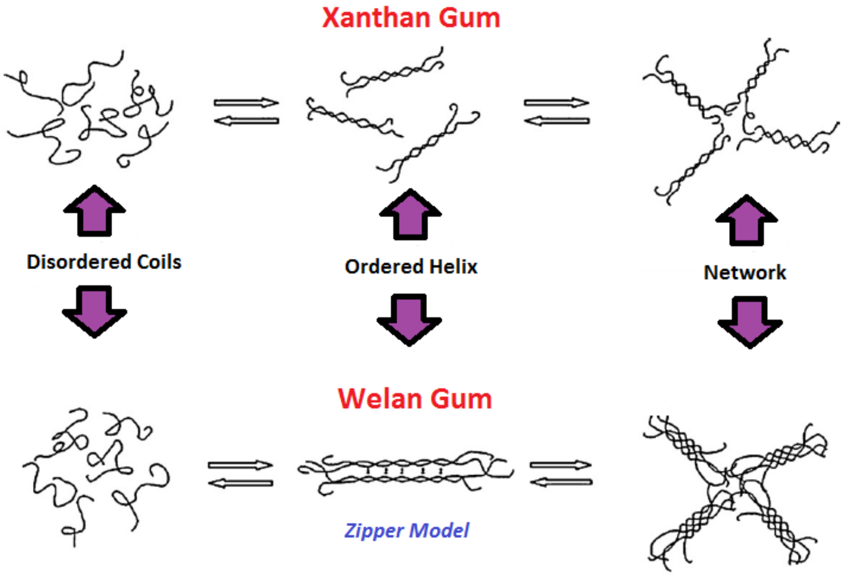


Figure 1.8 *Structural transitions of Xanthan and Welan Gum in Solution (Adapted from Xu et al. 2013)*

Scleroglucan gum:

Scleroglucan is a non-ionic branched exopolysaccharide produced by fermentation of a plant fungus genus *Sclerotium,* known to employ exceptional viscosifying properties in solution capable of withstanding harsh reservoir conditions (Kulawardana et al. 2012). It enhances the lubrication and cleaning ability of water-based muds, and is especially suited for use in deviated wells (Caenn, Darley and Gray 2011). Aside from its shear thinning characteristics, Scleroglucan has a higher thermal tolerance compared to similar polysaccharides as it forms a linear triple helical structure when dissolved in solution (see **Figure 1.9**), allowing the glucose side groups to extend and prevent aggregation, or gelling (Survase et al. 2007). In fact, from a study of over 140 polymers proposed for enhanced oil recovery use in North Sea reservoirs; scleroglucan was identified as the most temperature stable in seawater (Brigand 1993).

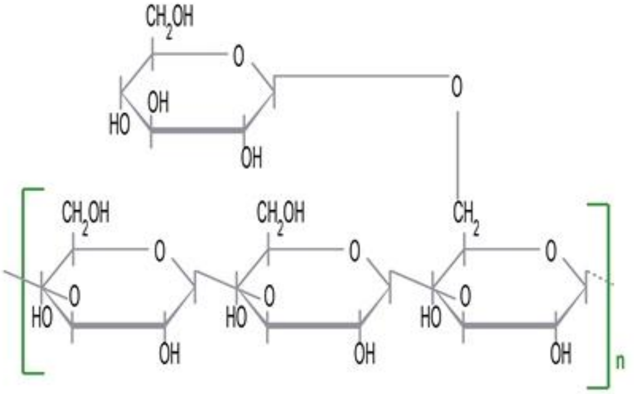


Figure 1.9 *The primary structure of Scleroglucan gum (Adapted from Survase et al. 2007)*

Guar gum:

Guar gum is a non-ionic, branched chain polysaccharide derived from refined endosperms of cluster bean seeds, chemically known as the galactomannans. It is typical in industry to create derivatives of conventional guar to improve characteristics for specific applications, such as hydraulic fracturing (Darley and Gray 2011).

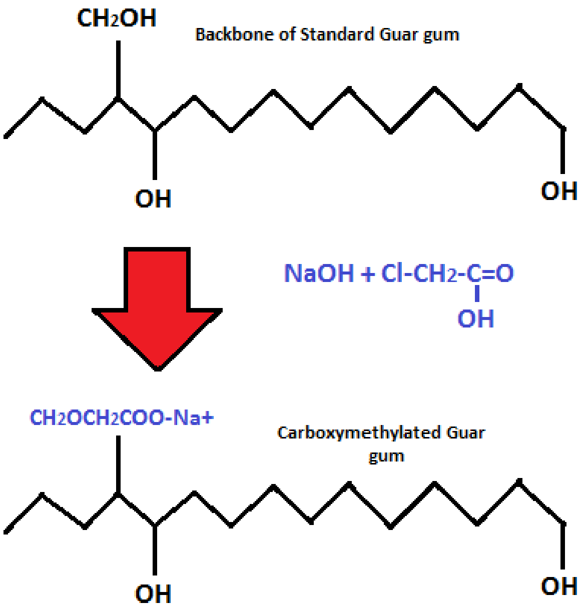


Figure 1.10 *Carboxymethylation reaction process of guar gum with sodium hydroxide and chloroacetic acid (Adapted from Dodi, Hritcu and Popa 2011)*

Carboxymethylation of guar and other "bio gums" increases their hydrophilic nature (or solubility in water) by introducing a sodium counter-ion and thus rendering the polymer slightly anionic. This method also reduces insoluble residues normally present in the standard guar which can be present at as much as 10-14% concentration depending on the gum purity. **Figure 1.10** depicts a common process method for the carboxymethylation of guar gum (Dodi, Hritcu and Popa 2011). The negatively charged carboxymethyl groups will repel each other and cause the molecule to occupy a larger hydrodynamic volume than it would do in the absence of charges, for example in standard guar gum. However, de-ionized water will maximise this repulsion, whereas addition of salts will screen the sodium counter-ion and lessen the electrostatic interaction leading to decreased solution viscosity (Lei and Clark 2004).

Guar gum can also produce extremely viscous suspensions for use in hydraulic fracturing or similar applications at low concentrations when combined with various cross-linking agents, for example borate, titanium and zirconate compounds. Typically, borate based cross linkers achieve higher viscosities with standard guar i.e. not chemically modified, whereas metal based compounds are more suitable for modified guars with a slight ionic charge, such as carboxymethyl guar, hydroxymethyl guar etc. (Deysarkar et al. 2011).

Xanthan gum:

Xanthan gum is a naturally occurring polysaccharide biopolymer produced from the bacterial coat of *Xanthomonas campestris* and used in a wide variety of industry applications; such as in food, pharmaceuticals, agriculture, textiles, cosmetics and water-based drilling fluids (García-Ochoa et al. 2000). In drilling fluids, xanthan gums primary role is suspension and mobility control, but is particularly effective as it imparts highly shear thinning characteristics allowing faster drilling by maintaining a low viscosity at higher pump rates, while thickening instantaneously if drilling is discontinued. This is a prime example of pseudoplastic rheological flow.

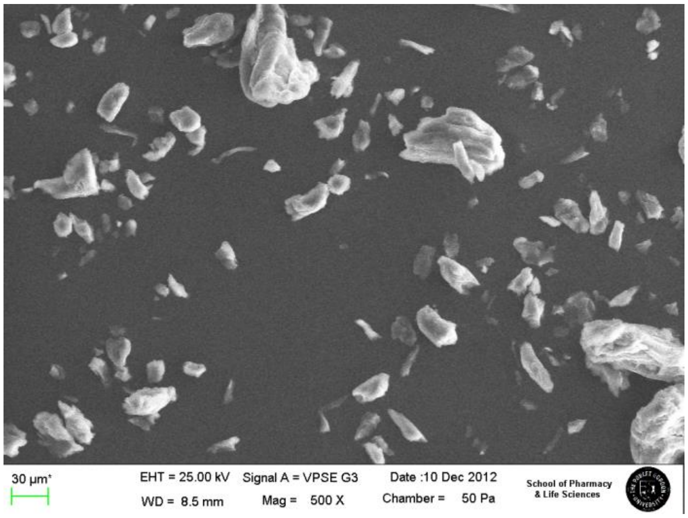


Figure 1.11 *SEM photograph of commercially available powdered xanthan gum (Xanvis®) for use in drilling fluids*

The shear thinning behaviour of xanthan in solution is a result of weak intermolecular attractions within the polymer chain to form a complex network of rod-like molecules (see **Figure 1.11**). The polymers backbone is made up of a number of glucose monomers connected by β(1-4) glycosidic linkages, with a charged trisaccharide side chain at every second unit (see **Figure 1.12**) which in solution can wrap around its cellulosic backbone and protect it from oxidative and hydrolytic attack. Various studies have demonstrated that the modification of fermentation conditions (such as Xanthomonos strain, medium used, temperature and pH) during xanthan production can alter the overall molecular weight and functionality of side chains in controlling viscoelastic properties in solution (Downs 1991; (Garcı́a-Ochoa et al. 2000; Norton, Spyropoulos and Cox 2010). In particular, the effect of acetate and pyruvate groups in the anionic trisaccharide side chain is probably the most extensively studied in terms of structure-function relationship. Seright & Henrici, 1990 along with others have stated that altering the ratios of ketal-linked pyruvate and O-acetyl groups which can be affected during production significantly influence rheology and melting temperature (T_m) of xanthan in solution; the order-disorder molecular transition by which a sudden loss in viscosity is experienced (Seright and Henrici 1990). To benefit high temperature applications, other researchers recorded the highest transition temperatures in xanthan molecules containing minimum pyruvate and maximum acetate groups in their trisaccharide chain (Glass et al. 1983; Downs 1991; Renou et al. 2013). Optimized synthesis of pyruvate and acetate groups can also determine how the biopolymer interacts synergistically with other polymer molecules to form a viscous solution for example, with the gallactomannans such as locus bean gum and guar gum (Fink 2011; Renou et al. 2013).

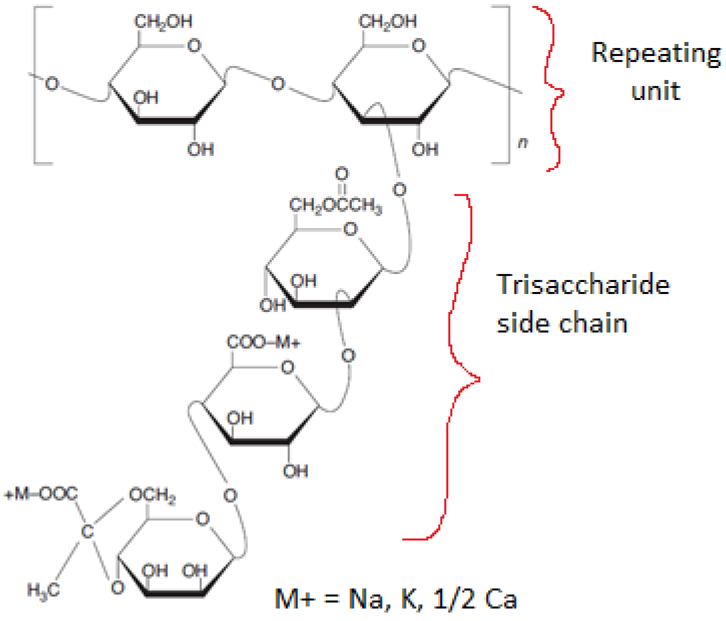


Figure 1.12 *illustrates the primary structure of xanthan (Adapted from Norton, Spyropoulos and Cox 2010)*

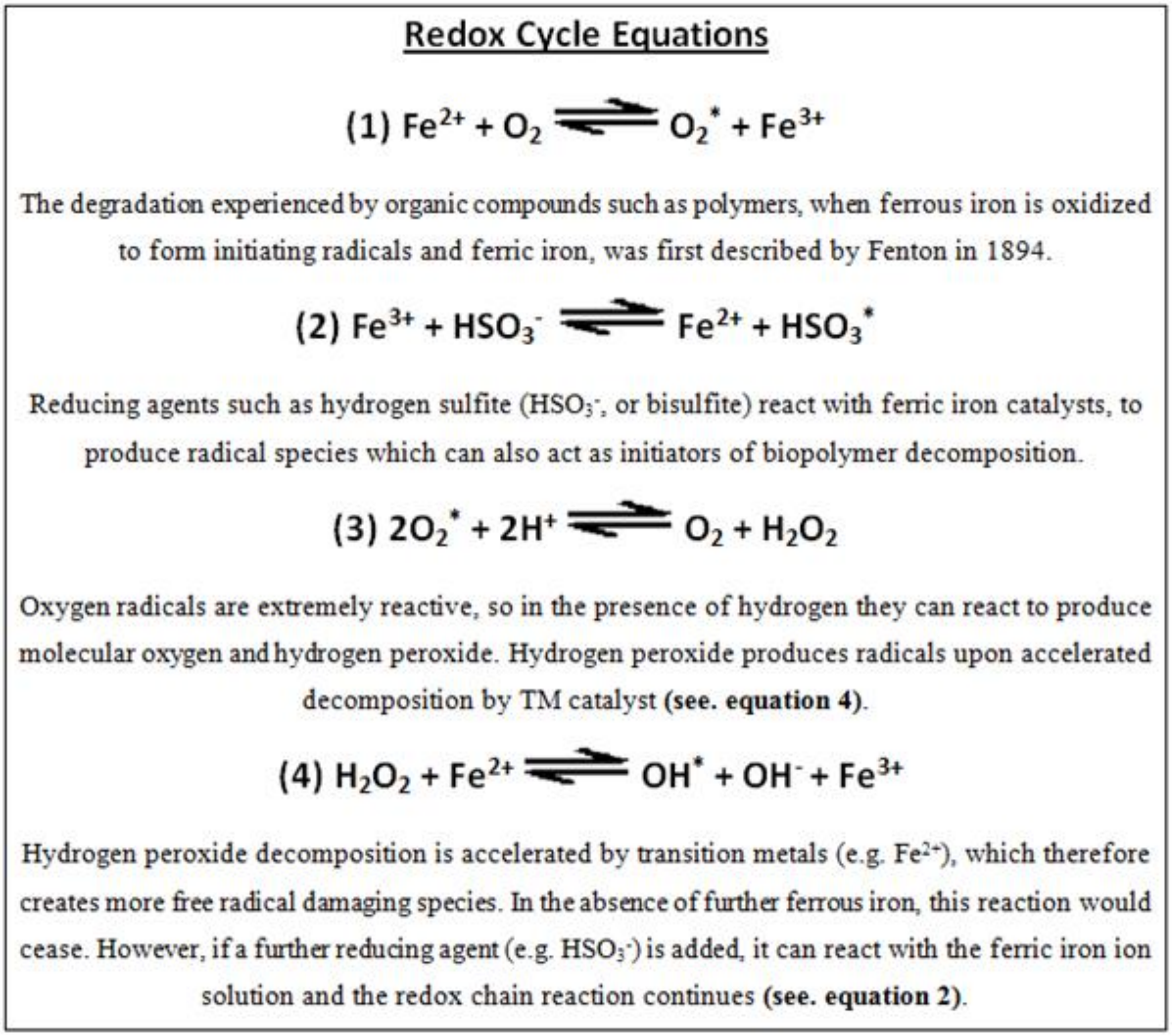
In addition to fermentation and operational conditions, other factors which can alter xanthan properties in solution are; pH, biopolymer concentration, salt concentration and temperature. Since xanthan is an anionic polymer, lowering or increasing pH will alter the overall charge density, influencing molecular associations to increase or reduce the stiffness of the molecules resulting in a notable change in viscosity (Norton, Spyropoulos and Cox 2010). This effect however is completely reversible upon neutralization so polymer decay is not evident varying pH *at ambient conditions*, only changes in molecular conformation. Consequently, most authors agree that the optimum pH for xanthan hydration and viscosity is pH 7 (Seright and Henrici 1990; Glass et al. 1983).

With regards to xanthan concentration, normally viscosity sharply increases with additional polymer due to increased electrostatic interaction and cross-linking between the chains. However, the transition of xanthan gum from the ordered helical structure promoted by hydrogen bonding, to the less stable coil conformation occurs independently of xanthan concentration (although T_m may be more prominent in highly viscous solutions). The stability and order-disorder conformational transition of xanthan gum is particularly affected by temperature and ionic concentration in solution (García-Ochoa et al. 2000). In general, higher stability and transition temperatures are measured when xanthan is hydrated in highly saline solutions rather than in de-ionized water; the excess dissolved salts forces increased associations between the charged xanthan molecules and favours the ordered more rigid helical structure which can shield the glycosidic polymer backbone. With that said, it has been well documented in literature that the temperature at which the helix to random coil transition occurs is far lower in the presence of divalent ions than monovalent; for example a significantly lower T_m can be observed in calcium chloride ($CaCl_2$) solution compared with sodium chloride (NaCl) or any highly concentrated formate brine e.g. CsCOOH, KCOOH or NaCOOH. In fact, the transition temperature of xanthan in formate brines can reach as high as 200ºC in the case of saturated potassium formate (Seright and Henrici 1990; Howard 2009).

In order to provide maximum long-term stability of xanthan gum for high temperature applications, it is essential to understand probable degradation mechanisms and implement products or methods to counteract destructive influences which can lead to polymer decomposition. The most prevalent mechanisms for xanthan degradation at high temperatures include; oxidation-reduction (redox) reactions, early onset of the helix-coil conformational transition and dependent on pH, acid-catalysed hydrolysis of the terminal β-mannose /base fragmentation reactions; or any combination of the above (Seright and Henrici 1990).

1.3.4 Polymer Degradation Mechanisms and Stabilizing Additives

Oxidative degradation of xanthan gum and other drilling and completion polymers is of great industry concern, as dissolved oxygen from the atmosphere is unavoidable in field polymer solutions and produces destructive radical species in the absence of an effective oxygen scavenger. In the case of polysaccharides such as xanthan and scleroglucan gum, the depolarization of the carbon-hydrogen bond between acetyl oxygen linkages allows dissolved oxygen in solution to thermally oxidize hydrogen setting up a redox cycle, and thereby promoting chain scission of the polymer backbone and a consequent reduction in molecular weight (Ash et al. 1983). In association with oxygen, the presence of transition metals (TM) in oxidizable states such as Co^{2+}, Cu^{2+}, Mn^{2+}, Cr^{2+}, V^{2+} and Fe^{2+} in solution with susceptible polymer molecules, strongly contribute to radical degradation by redox cycling metals – metals which oxidize by a two-electron transfer, are not as destructive to the polymer (tin, thallium etc.). Traces of metal ions are already present in most biopolymers, however, the predominant metal cation in petroleum recovery processes for oxidative degradation is Fe^{2+} usually obtained from exposure to steel, also known as the Fenton reagent, or ferrous iron. **Figure 1.13** illustrates many common reaction mechanisms for redox cycling in oxidation-reduction depolymerisation (Glass et al. 1983; Wellington 1983).



Redox Cycle Equations

$$(1)\ Fe^{2+} + O_2 \rightleftharpoons O_2^{*} + Fe^{3+}$$

The degradation experienced by organic compounds such as polymers, when ferrous iron is oxidized to form initiating radicals and ferric iron, was first described by Fenton in 1894.

$$(2)\ Fe^{3+} + HSO_3^{-} \rightleftharpoons Fe^{2+} + HSO_3^{*}$$

Reducing agents such as hydrogen sulfite (HSO_3^-, or bisulfite) react with ferric iron catalysts, to produce radical species which can also act as initiators of biopolymer decomposition.

$$(3)\ 2O_2^{*} + 2H^{+} \rightleftharpoons O_2 + H_2O_2$$

Oxygen radicals are extremely reactive, so in the presence of hydrogen they can react to produce molecular oxygen and hydrogen peroxide. Hydrogen peroxide produces radicals upon accelerated decomposition by TM catalyst **(see. equation 4)**.

$$(4)\ H_2O_2 + Fe^{2+} \rightleftharpoons OH^{*} + OH^{-} + Fe^{3+}$$

Hydrogen peroxide decomposition is accelerated by transition metals (e.g. Fe^{2+}), which therefore creates more free radical damaging species. In the absence of further ferrous iron, this reaction would cease. However, if a further reducing agent (e.g. HSO_3^-) is added, it can react with the ferric iron ion solution and the redox chain reaction continues **(see. equation 2)**.

Figure 1.11 *Redox Reactions for Radical Degradation*

In many drilling and completion applications, it is customary to add oxygen scavengers (or reducing agents) to water-based fluids to eradicate excess oxygen in solution, to reduce corrosion of equipment and inhibit oxidation of the biopolymer. However, the difficulty with reducing agents (e.g. hydrogen sulphite HSO_3^-) when used to remove dissolved oxygen is they can also contribute to biopolymer decomposition by producing initiating radical species as reaction intermediates, which allows degradation to occur more rapidly especially if a new source of oxygen is leaked into the system (**Figure 1.13:** equation 2). In addition, the use of oxygen scavengers promotes lower valence states of TM catalysts which in turn, slowly churn out free radicals as part of the redox cycle (**Figure 1.13:**

equation 1, 2 &4) (Wellington 1983; Levitt et al. 2011). Due to above limitations, it is important that the preferred thermal stabilizer is compatible with its organic chemistry application and the dosage is adjusted according to field conditions.

Since reducing agents react with dissolved oxygen to remove it from the system, the anti-oxidant stabilizers function in a similar manner through inhibiting the oxidation depolymerisation process. The two main categories of anti-oxidants commonly used to prevent corrosion and premature polymer degradation in the oilfield are; primary "chain-breakers" and secondary "preventative" type products. Chain-breaking antioxidants intervene directly in the oxidation process, and preventative antioxidants disrupt the formation of radicals by producing stable products in reaction with hydrogen peroxide. However, Wellington *et al*., 1983 recommended that secondary preventative anti-oxidants were more effective in deterring biopolymer decomposition particularly in oil-recovery applications (Levitt et al. 2011; Rychlý and Matisová-Rychlá).

As mentioned earlier, pH is a large determining factor in influencing rate of degradation of polymers. Generally, biopolymers are more stable in slightly basic conditions rather than acidic, however at pH 12 and above; de-acetylation can occur even at room temperature in an aqueous solution. Removal of acetyl groups, leads to a decrease in conformational transition temperature and results in lower stability so it is important to ensure pH remains within recommended range (Glass et al. 1983). After de-acetylation, the next most probable group susceptible to attack on the side chain is pyruvate, where its principle pathway for degradation is through acid catalysed hydrolysis, along with the vital β-glycosidic sugar linkages. To avoid biopolymer decomposition related to uncontrollable pH, a buffer system can be introduced; to ensure pH remains within the recommended range.

Several researchers have demonstrated that carbonate/bicarbonate buffer systems present in solution can potentially minimize polymer degradation due to their effect on decreasing iron solubility, inhibiting the oxidation of ferrous to ferric iron (**Figure 1.13:** equation 2) (Levitt et al. 2011). Also, since oxidation-reduction decomposition products are acidic, this would aid in the hydrolysis of biopolymer were the solution not neutralized in some way (Howard and Downs 2009; Glass et al. 1983). In disagreement however, Seright & Henrici, 1990 proposed that various buffers can actually destabilize xanthan’s preferential helical structure at high temperatures, but carbonate/bicarbonate systems were not tested – only phosphates, tris, imidazole’s and hepes (Seright and Henrici 1990).

1.3.5 Synthetics

The advantages of biopolymers over synthetic materials used in drilling and completion fluids, are they are more ecological being biodegradable, have increased resistance towards mechanical degradation and demonstrate strong shear thinning properties. However, an ongoing issue is polymer burning and carbonization at high down-hole temperatures, which ultimately leads to total destruction of the biopolymer material and complete loss of viscosity function. Therefore, in an effort to improve temperature stabilization of polymer muds, numerous water dispersible synthetic polymers based on monomeric materials can be employed.

Most synthetic polymers for use in drilling or completion fluids are composed of thermally stable monomers designed to minimize hydrolysis and other oxidative process that degrade the polymer backbone (Ezell et al. 2010). There are many different approaches to the design of synthetic polymers, to exhibit improved stability for the specific environment. Generally, the introduction of the listed groups and structures are targeted in the manufacturing and synthesis process to enhance polymer properties;

- Introduction of ring structure,
- Introduction of large side groups or rigid side groups e.g. acrylamide,
- Introduction of a high salt tolerant group e.g. AMPS,
- Introduction of a hydrolysis resistant group,
- Introduction of groups that can inhibit hydrolysis of amine e.g. NVP, AMPS and,

- Introduction of hydrophobic groups, e.g. acrylic dodecyl ester, N-alkyl acrylamide (Wu et al. 2012).

Adopting for a polyacrylamide-based structure for further synthetic integration is also common as it lacks the glycosidic bonds of polysaccharides which are more easily targeted by hydrolysis and oxidative degradation processes that occur at high temperatures. In fact, Holtzlaw and Funkhouser, 2010 developed a high temperature cross-linkable fracturing fluid based on an acrylamide terpolymer, which is capable of maintaining stability up to 232°C to overcome the thermal limitations of guar based derivatives (Holtsclaw and Funkhouser 2010).

1.4 Aims and Objectives

The main aim of this project was to develop a well construction fluid based on organic brine (caesium/potassium formate) which can exceed temperature restrictions of thermally stable systems already utilized in oilfield applications.

Initial Objectives proposed for this project were:

1. Measure base brine viscosities in the four alkali metal formates; sodium, potassium, rubidium, caesium formate and caesium acetate. By doing so, we can evaluate the true polymer yield and determine how much to add in order to obtain a certain viscosity threshold in each brine.

2. Measure xanthan stability and T_m in the four alkali metal formates; sodium, potassium, caesium formate and caesium acetate.

3. Investigate temperature stabilities for xanthan gum in standard caesium/potassium formate blends; construct a graph to evaluate an optimum blend. Add thermal extenders/anti-oxidants/cross-linkers to optimum formulation to enhance stability further.

4. Evaluate new HPHT synthetic polymers which have not been previously researched in formate brine and assess their performance with regards to temperature stability.

5. Analyze successive HPHT polymers in combination with other biopolymers/additives to examine synergistic reactions that may occur for example, cross-linking mechanisms which produce stabilizing effects.

The further objectives are listed below.

6. Qualifying the various grades of commercially available xanthan grades in caesium/potassium formate brine and investigate the most temperature resistant brand to exercise in further stability studies. From

this preliminary investigation, it was determined that Xanvis® from CP Kelco is the most stable at high temperatures.

7. Investigate the compatibilities of biopolymers, such as xanthan, guar, carboxymethyl guar, welan and scleroglucan gum in Cs/K formate brine and evaluate overall temperature stability and potential T_m measurements for each.

8. Discover alternative hydration methods for biopolymers in Cs/K formate brine for example, altering buffer and/or pH, adding product in liquid form or applying heat.

9. Consider xanthan hydration in formate brines, and how solution viscosity can be affected by alternating the base brine.

10. Compare xanthan properties in caesium and potassium formate brines on a molar basis, and observe the effect of exchanging the cation.

11. Evaluate pH and buffer effects on the hydration and stability of xanthan gum in caesium and potassium formate brines.

12. Create a well construction fluid, consisting of Cs/K formate brine, biopolymer and synthetic material which will be thermally stable at ultra-HPHT temperatures.

Additionally, other relevant topics which have not been examined in Results and Discussion but were published externally during the course of the MRes project are catalogued below:

13. Viscosifying caesium-weighted glycol fluids with water-soluble polymers and evaluating their own temperature stability limits. This idea materialized from discovering that formate salts can dissolve in non-

aqueous solvents or glycols to produce high density novel well-construction fluids (See **Clearly Different** article in Appendix).

14. Formates used in combination with clouding glycols (e.g. polyethylene glycol) to improve shale stabilization used while drilling the intermediate section of a well. Formate salts in aqueous solution with glycols are TAME (thermally activated micro emulsion) fluids which reduce cloud point temperature further than the standard monovalent brines such as KCl, NaCl etc., and extend these brines capabilities as competitive well-construction fluids in the field. Using varying formate salt and glycol concentrations, a TAME fluid can be developed for the operators required application (see **Clearly Cloudy** article in Appendix).

Chapter 2 : Methodology and Quality Control

This chapter introduces the experimental methods applied during this project and information regarding the relevant instruments. The methods included in this chapter are; measuring pH in Formate brines, measuring carbonate/bicarbonate buffer content, removing buffer content, hydrating polymers in solution, mixing a formate drilling mud, Fann35 viscometer, dynamic ageing, measuring 50% viscosity loss and 16-hr stability, measuring $T_{50\%}$ using MARS III rheometer data, measuring transition temperatures of biopolymers in solution and calculating apparent viscosity using Fann35 readings.

The detailed operational procedures are described in the following sections.

Table 2.1 Instrumentation and their functions as employed in this project

Instruments	Manufacturer	Function
Silverson High Shear Mixer	Silverson Machines, Buckinghamshire, UK	Mud shearing
Paddle mixer	OFI Testing Equipment Inc. Houston, USA	Mud mixing
DM-40 density meter	Mettler Toledo, Columbus	Brine density measurement
Hotplate stirrer	Scientific Laboratory Supplier	Solution mixing
pH meter	Mettler Toledo, Columbus	pH value measurement
HPHT hot rolling oven	OFI Testing Equipment Inc. Houston, USA	Dynamic ageing
Fann 35A rheometer	OFI Testing Equipment Inc. Houston, USA	Rheology measurement
MARS III HPHT Rheometer	Thermofisher Scientific, Karlsruhe, Germany	HPHT Rheology measurement

2.1 Experimental Methods and Procedures

2.1.1 Measuring pH in Formate Brines

Normally, pH is measured on "neat" samples, however in highly concentrated brines the hydrogen ion (H^+) activity varies significantly from the H^+ concentration so a true pH cannot be determined using conventional pH meters. Therefore, for a better estimation of pH in a formate fluid, it is diluted by nine parts de-ionized water to gain a closer representative pH value - although it is still not absolute (Howard 2010). This is measured using a Mettler Toledo Seven-multi pH electrode meter (see **Figure 2.1**).

Figure 2.1 *Mettler Toledo glass electrode pH meter (photograph taken in CSF Laboratory)*

2.1.2 Measuring Carbonate/Bicarbonate Buffer Content

To determine the concentration of carbonate and bicarbonate in a formate fluid, a phenolphthalein end-point titration is used. To begin, pH is measured by electrode meter after diluting the formate by nine parts de-ionized water. If the pH is above 9, a couple drops of phenolphthalein indicator should be added to turn the solution pink and titrate back to initial clear colour (or pH 8.2) using 0.2N HCl – recording the volume required to do so. If pH is below 9, record initial pH and increase to above 10 with 8N potassium hydroxide and titrate the same as above- remembering to record the volume of KOH used and adjusted pH.

To calculate the amount of carbonate and bicarbonate in mol/L or ppb (grams per 350mL), the **Buffering Capacity (phenolphthalein) Calculations** spreadsheet is used or alternatively, if the pH needs to be lowered; the **Carbonate/Bicarbonate Determination V7 Jan 13 – with KOH**.

2.1.3 Removing Buffer Content

The method used for removing potassium carbonate/bicarbonate in caesium formate is to drop the pH from around 10.1 to below 6 using formic acid, which consumes the buffer completely and bubbles off as CO_2 gas. If pH is to be increased again, caesium hydroxide (50%) is used in caesium formate and potassium hydroxide (8N) is employed for potassium formate.

2.1.4 Hydrating Polymers in Solution

In the drilling fluids industry, water-soluble polymers are mixed into solution and sheared by action of the drill bit to promote further hydration. This is simulated in the laboratory by using a Silverson mixer, with a specialized shear head designed for optimum hydration of polymers in water-based fluids.

Figure 2.2 *Silverson mixer (left) and shearing head (right) for water-based drilling fluids*

Fluids are mixed in equal volumes, so 4 lab bbls (or 1400mL) to ensure uniformity and mixed in 2L stainless steel mixing jugs at 6000 rpm for a total of 45 minutes. For tests in the current study, polymers were slowly added to the brine at the start of the mix and any other chemical stabilizers were added 5 minutes after.

2.1.5 Mixing a Formate Drilling Mud

To prepare a complete formate drilling fluid, the same principles apply as **2.1.4**, i.e. the fluid is mixed in 4 lab bbl volumes at 6000rpm for 45 minutes using a water-based mud shearing head (**Figure 2.2**). However, in addition to the primary viscosifier, further products required to produce ideal mud properties, must be added in the correct order, according the API (American Petroleum Institute) guidelines.

***Mixing Order:**

Additive	Mixing Time
Brine	0 minutes
Polymers	5 minutes
Fluid Loss Additives	10 minutes
Thermal Stabilizers	15 minutes
Bridging Solids (calcium carbonate)	40 minutes

*Mud temperature should not be allowed to exceed 66ºC; if the temperature nears this point, water should be added to the jug the mud sits in to control the temperature to between 60 and 66ºC.

For addition of bridging solids; to reduce further breakdown of particles, stop the mix and remove the shear head before adding, and apply enough force to allow for appropriate distribution of the calcium carbonate – around 5 minutes. Also, it is essential that all additives are added in slowly, especially if using magnesium oxide as a thermal stabilizer as it has the potential to "burn" the polymers if added in too quickly.

2.1.6 Fann35 Viscometer

The Fann35 rotational viscometer is a Couette coaxial cylinder which directly measures shear stress as a function of shear rate at six different variable speeds (from 3 - 600rpm), which is particularly useful for measuring thixotropic fluids, such as drilling muds. The test fluid is contained in the annular gap between the outer cylinder and bob, and viscosity measurements are made when the outer cylinder rotating at a known velocity (or shear rate), causes a viscous drag to be exerted by the fluid. This drag creates a torque on the bob, which is transmitted to a precision spring where its deflection is measured.

Figure 2.3 *Fann35 Viscometer (Photograph taken in CSF Laboratory)*

These instruments have been designed so that apparent viscosity in centipoise (cP) or milli Pascal seconds (m.Pas) is indicated on the dial with the standard rotor, bob and torsion spring operating at 300rpm. Viscosities at other test speeds can be measured by using multipliers of the dial reading.

Procedure:

- The sample is placed in the stainless steel measuring cup and the rotor sleeve is immersed in the liquid to the 350mL scribed line, to ensure two holes on the rotor are completely covered with fluid. The sample should shear at around 300 or 600rpm until the temperature is stable at 50ºC (this should take around 5-10 minutes).
- With the sleeve rotating at 600rpm, the viscometer dial reading is recorded when a steady value is reached – if there are much larger particles in the fluid such as loss circulation material, they may cause erratic results.
- The rotor speed is reduced to 300rpm, and dial reading is recorded again once a steady value has been reached. This same motion is repeated at the lower shear rates, 200, 100, 6 and 3 rpm.
- To record gel strengths, the shear rate is increased to 600rpm for around 10 seconds, and then stopped so the drilling fluid remains undisturbed for 10 seconds. The rotor is switched back on to low shear (3rpm) and the

maximum dial reading is recorded. For the 10 minute gel, the same procedure is adopted, but for 10 minutes instead of 10 seconds, and the maximum dial reading is recorded in pounds per $100ft^2$.

2.1.7 Dynamic Ageing

To determine the effect of thermal ageing on mud properties, the fluid is added to temperature resistant alloy cells, pressurized with nitrogen to >200psi and "rolled" in specialized ovens for 16 hours at allocated temperatures. This is known as "hot-rolling" or dynamic ageing and is used to simulate the circulation of the fluid exposed to various temperature conditions in the field. A recently prepared mix which has not been exposed to heat can be described as a before-hot rolled (BHR) fluid and after dynamic ageing for 16 hours can be distinguished as after hot-rolled (AHR).

Figure 2.4 *Temperature resistant cell for dynamic ageing (left) and inside a hot-rolling oven (right), CSF Laboratory, Aberdeen*

Testing includes; Fann35 rheologies and pH before and after ageing, to measure temperature effects on the polymer and/or other additives combined.

2.1.8 Measuring 50% Viscosity Loss and 16-Hr Stability

The following method was used to estimate the fluids long term (16-hr) stability limit; measuring **50% viscosity loss** in relation to the starting viscosity. Recording initial brine viscosities and subtracting them from the starting viscosity or "viscosity after xanthan addition," eliminates them from the equation, so as to solely calculate the effect of xanthan;

50% viscosity loss = Viscosity after xanthan addition –

Viscosity before xanthan addition / 2

+ Viscosity before xanthan addition

Initial brine viscosities or "viscosity before xanthan addition" must be added back onto the end result. Using the above equation, 50% viscosity loss can be calculated to estimate the maximum 16 hour stability temperature using the example in **Figure 2.5**.

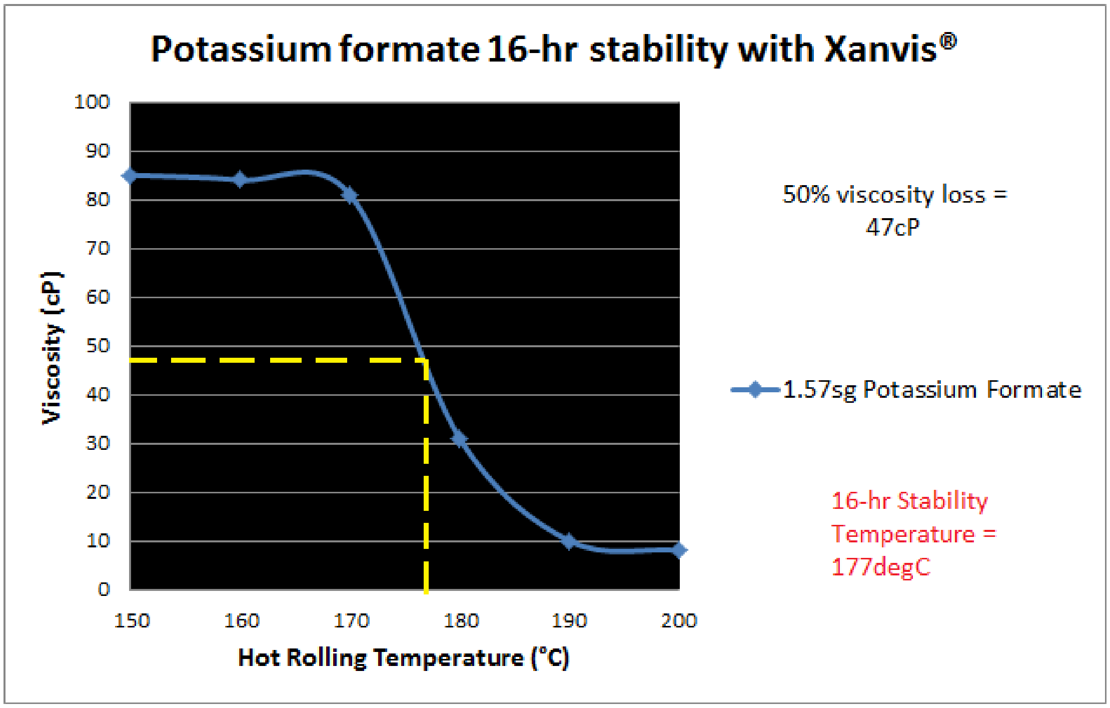


Figure 2.5 *Xanthan Stability (16-hr) in Potassium formate brine – example of how to measure 50% viscosity loss and 16-hr stability limit*

Figure 2.5 illustrates the shear stress in lb/100ft^2 equivalents to viscosity in cP at 511s^{-1} shear rate reading on Fann35 viscometer measured at 50ºC as a standard, plotted after hot-rolling at the various temperatures for 16 hours. The points at 150ºC can be described as the fluids starting viscosity or "viscosity after xanthan addition" to determine 50% viscosity loss. The reason initial rheology is not used as the starting viscosity is because the biopolymer needs heat and time to fully hydrate in salt solutions, and it is difficult to accomplish repeatable data before hot-rolling (except in the case of de-ionized water) – higher consistency in results for xanthan in brine can be achieved once the fluid has been hot-rolled for at least 16 hours.

2.1.9 Measuring T50% or 50% Viscosity Loss Temperature using MARS III Rheometer Data

Figure 2.6 *Haake MARS III HPHT Rheometer (Photograph taken in CSF Laboratory)*

To measure $T_{50\%}$ using data from the MARS III Rheometer;

*$T_{50\%}$ = Starting viscosity of BHR polymeric fluid in cP (or viscosity @ 25ºC) (**Figures 3.4, 3.5 & 3.6**)*

*(minus [-]) Brine/Water viscosity in cP @ 50ºC (**Figure 2.7**)*

*(divided by [/]) 2 + Brine/Water viscosity in cP @ 100ºC (**Figure 2.7**)*

Then use these to work out the temperature at which this 50% viscosity loss ($T_{50\%}$) is experienced.

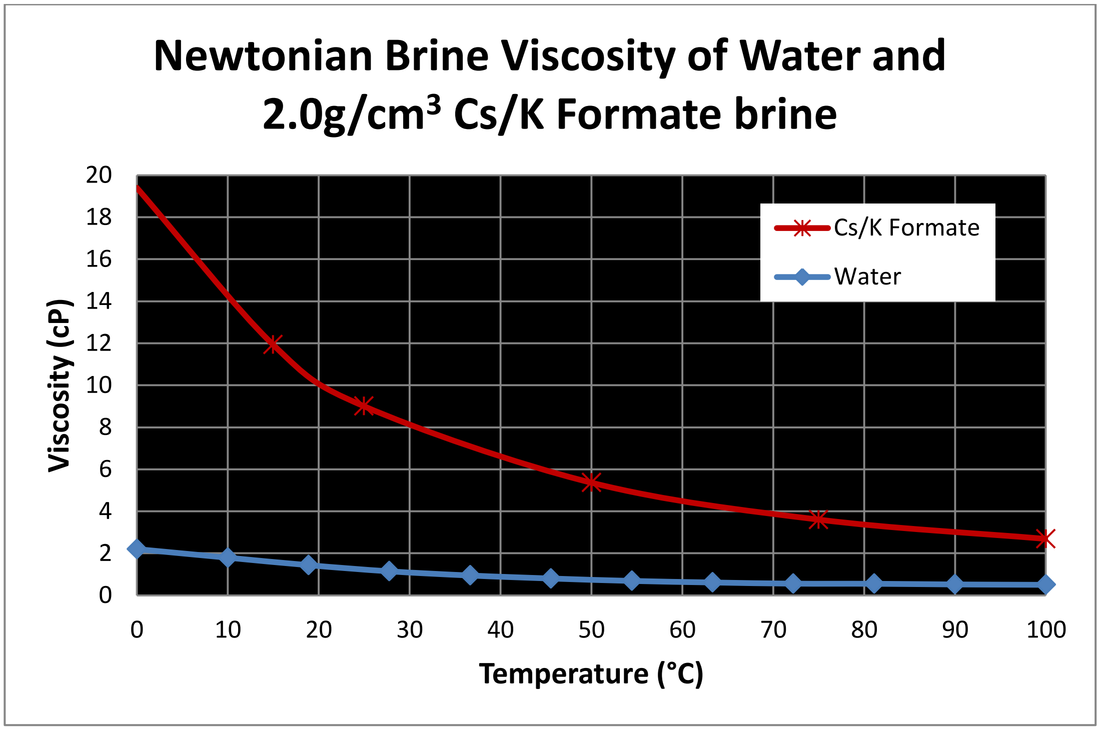


Figure 2.7 *Newtonian viscosities of 2.0g/cm^3 Cs/K formate brine and water for measuring $T_{50\%}$ (i.e. water is ~1cP at 50ºC and Cs/K formate is ~5.5cP and at 100ºC, water is 0.5cP and Cs/K formate is 2.5cP).*

The brine/water viscosity @ 100ºC is used as a standard to negate the Newtonian contribution at the higher temperatures even though it might be even less at $T_{50\%}$, the error should be negligible as the brine viscosity is relatively flat after 100ºC. This method is far more accurate than using the Newtonian viscosity @ 50ºC for both stages, as unlike the 16-hr stability tests which are all measured using Fann35 rheologies @ 50ºC; thermal thinning will influence the polymeric solution at higher temperatures.

2.1.10 Measuring Transition Temperature of Biopolymers in Solution

As discussed in the introduction, the transition temperature of biopolymers is known as the order-disorder conformational change at a critical transition or melting temperature (T_m) which results in a sudden drop in viscosity coupled with an increase in the rate of hydrolytic and oxidative degradation by two orders of magnitude.

Transition temperatures were measured using a Haake MARS III HPHT Rheometer and pressure cell measuring device. All tests were run using the "step-ramp" program icon at $500s^{-1}$ shear rate which corresponds roughly to the 300rpm ($511s^{-1}$) on a Fann35 viscometer. An integration time of 3 seconds for each test in the Haake Rheowin software was utilized for all transition temperature measurements to ensure consistency of results.

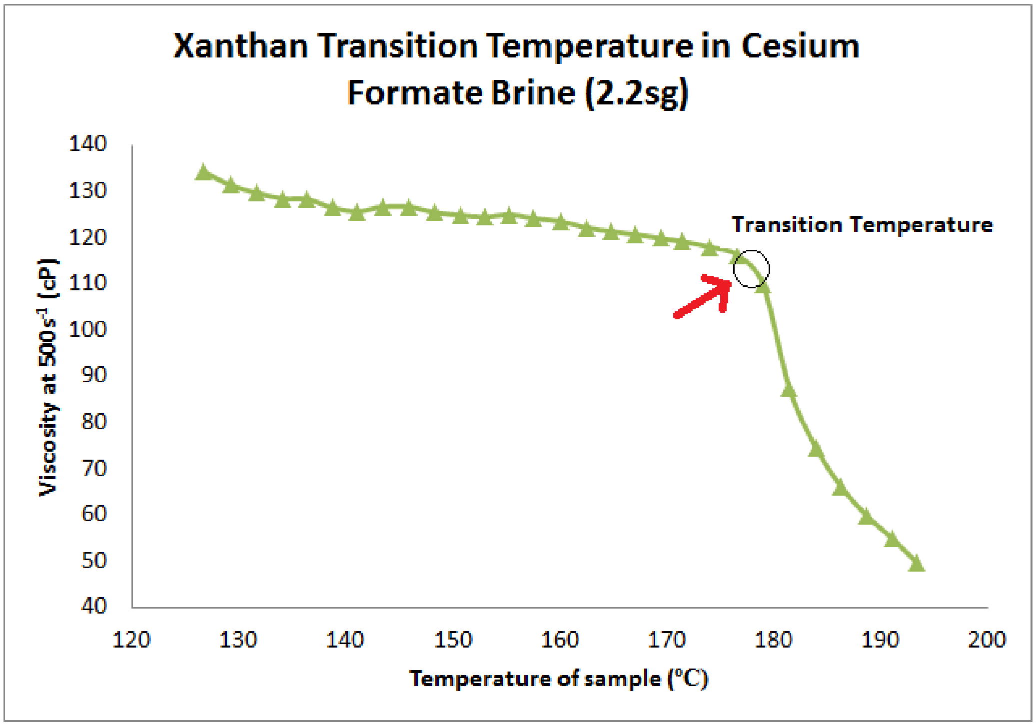


Figure 2.8 *Measuring transition temperature of xanthan in caesium formate (2.20g/cm^3) brine (buffer removed and low pH) on the Haake MARS III HPHT Rheometer*

Transition temperature of biopolymers (such as xanthan gum) is measured by constructing a graph of sample temperature (ºC) vs. viscosity at a constant shear rate (500s^{-1}), see example in **Figure 2.8**. The peak in the graph at which an immediate drop in viscosity can be observed, is noted as the transition temperature.

2.1.11 Calculating Apparent Viscosity Using Fann35 Readings

To calculate apparent viscosities;

Apparent Viscosity (cP) =

Shear stress (lb/100ft^2) x 511s^{-1} / Shear rate (s^{-1})

Table 2.2 can be utilized to convert shear rate units for apparent viscosity calculations to confirm shear thinning/shear thickening rheological behaviour in section **3.4**.

Table 2.2 Converting Fann35 Dial Readings into Shear Rate for Apparent Viscosity Calculation

To convert rpm to s^{-1}	
Dial Reading (rpm)	Shear Rate (s^{-1})
600	1022.0
300	511.0
200	340.7
100	170.3
6	10.2
3	5.1

2.2 Quality Assurance

2.2.1 Quality Control

MSDS (material safety data sheets) and work instructions, listed below were followed for all materials and methods specified in this project.

Cabot Specialty Fluids Work Instructions:

- WI-18: Water Activity of Brines
- WI-23: Cabot Laboratory Drilling Fluids Preparation
- WI-24: Determination of Carbonate and Bicarbonate Concentrations of a Formate Fluid
- WI-25: Pressurized Mud Balance
- WI-28: Filter Press – with N_2 or CO_2 Assembly
- WI-32: Fann35A Viscometer
- WI-35: Mettler Toledo Sevenmulti pH Meter
- WI-38: Thermal Ageing of Fluids Using Roller/Static Ovens
- WI-44: Mettler Toledo Benchtop Density meter (DM-40)
- WI-46: HPHT Filter Press Using Nitrogen

Haake MARS III Rheometer Handbook Instructions:

- Instruction Manual, Haake III MARS, Version 1.5
- Instruction Manual, Haake Pressure Cell D400/300, Version 1.5
- Instruction Manual, Software Haake Rheowin, Version 1.3

With regards to reproducibility, all Haake MARS III HPHT Rheometer and 16-hr stability dynamic ageing measurements were repeated at least once to ensure reliable results. Regularly used equipment, such as density and pH meters were calibrated daily, and ovens were calibrated on a monthly basis.

2.2.2 Materials

Caesium (2.20g/cm^3) and potassium formate (1.57g/cm^3) stock brines were sourced from Tanco in Canada along with the caesium acetate. Sodium formate brine was prepared using de-ionized water and analytical grade powder (99.8%) from Sigma-Aldrich to reach its desired density. All of the formates are naturally alkaline in nature, however on this occasion the stock potassium formate (1.57g/cm^3) has a pH in between 6-7, whereas concentrated caesium formate (2.20g/cm^3) has a pH of around 10-10.5. Stock potassium formate has no added buffer whereas the caesium formate stock has the equivalent of 17.1g/L potassium carbonate/bicarbonate buffer (13.3g/L K_2CO_3 and 5g/L $KHCO_3$). Caesium acetate stock at density 2.20g/cm^3 also has a pH of around 10 and contains similar buffer levels to the stock caesium formate, 12.2g/L K_2CO_3 and 6.8g/L $KHCO_3$. Analytical grade prepared sodium formate brine contains no buffer, with a pH 7-8 at 1.32g/cm^3.

Xanvis® is a Kelco product and was utilized for the majority of testing. All other chemicals and products used for analysis were available in CSF Laboratory Aberdeen, or acquired from external companies – which will be mentioned specifically in Results and Discussion.

Chapter 3 : Results and Discussion

3.1 Newtonian Viscosities of Formates

3.1.1 Viscosity of Caesium Formate Brine

Base brine viscosities of sodium, potassium and caesium formate brines were measured at varying densities using the HAKKE MARS III Rheometer. Temperature viscosity profiles were recorded for each of the three formates, as well as viscosity at 25ºC. The temperature viscosity profiles for several concentrations of caesium formate are shown in **Figure 3.1**.

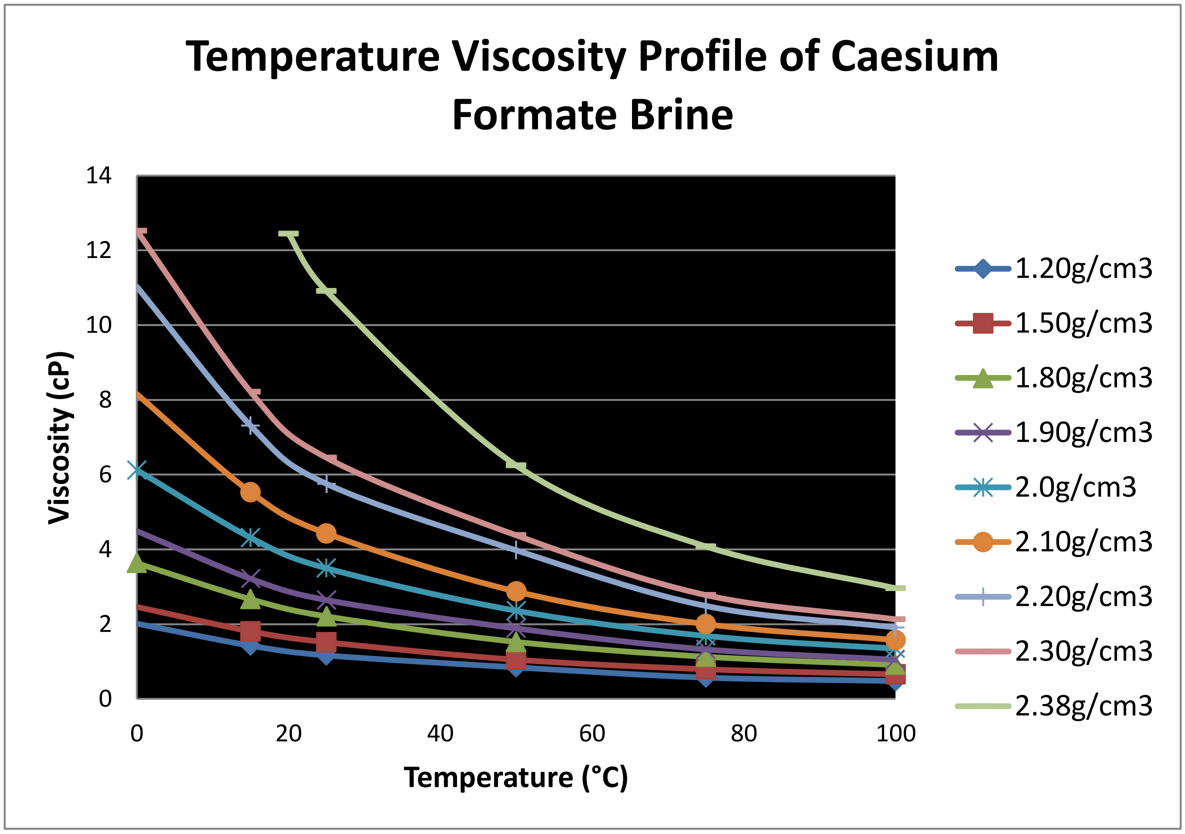


Figure 3.1 *Measured viscosity of caesium formate brine as function of density and temperature*

Figure 3.1 illustrates that the more concentrated caesium formate (higher density) results in a higher base brine viscosity, where thermal thinning is more apparent compared to the lower densities which have a relatively flat profile with regards to viscosity over 0-100ºC. The higher density brines contain more molecules per unit volume so are more closely packed together, therefore the forces between the molecules are far stronger than in the less concentrated brines, so a significant change in viscosity is measured as temperature decreases. This trend can also be observed with sodium and potassium formate brines along with all other Newtonian fluids.

3.1.2 Comparison of Viscosity Properties between Formate Brines

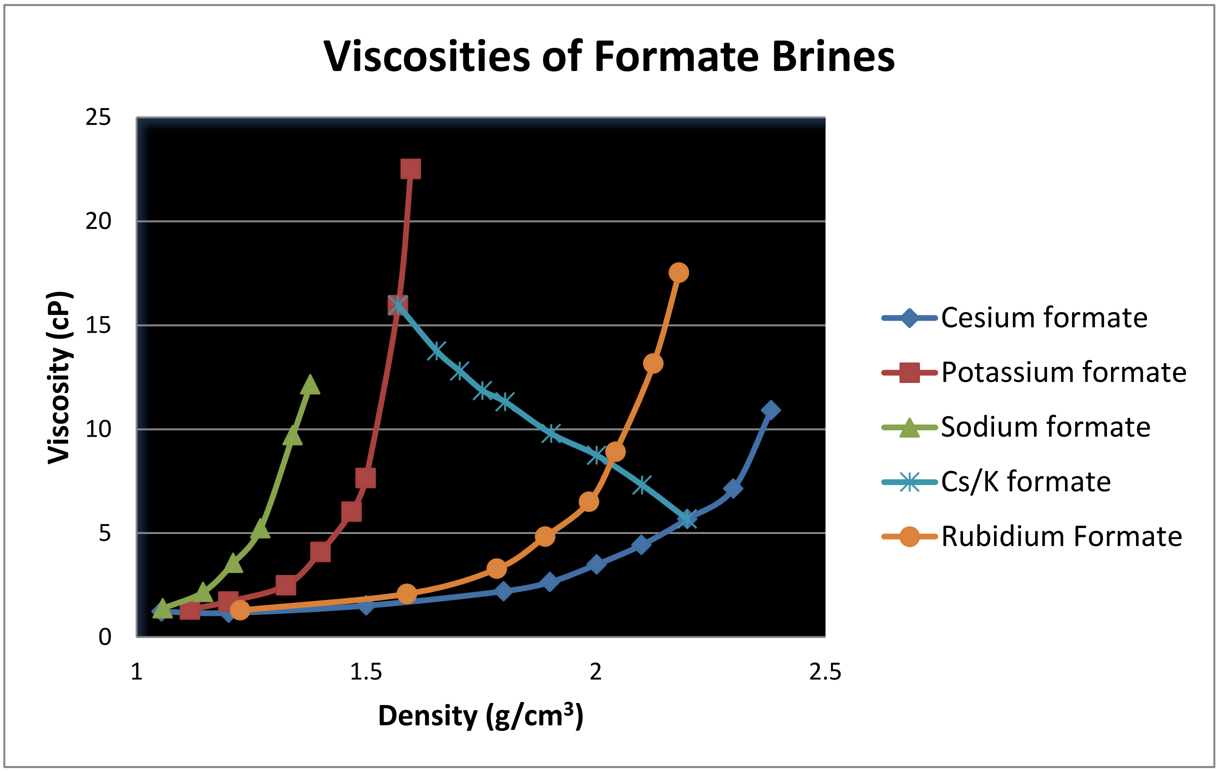


Figure 3.2 *Measured viscosity of sodium, potassium, rubidium, caesium formate and the caesium/potassium formate blends at 25ºC*

Figure 3.2 demonstrates the difference in viscosity between the four formates and a Cs/K formate blend. Caesium formate is the least viscous, even at super saturation (2.38 g/cm^3) its intrinsic viscosity is only 10.9 cP at 25ºC; less than sodium formate at only 1.38 g/cm^3. Sodium is the lightest of the three formates, so is highly saturated at this density. However, the slightly heavier potassium formate; although less viscous than sodium at the same density, achieves the highest viscosity of the alkali metal formates at full saturation, 22.5cP at around 1.60 g/cm^3. Rubidium formate, the least commercially available product of the four is only slightly more viscous than caesium formate – which may be beneficial to its potential uses in future applications within the drilling industry.

In addition, viscosities of caesium/potassium formate standard blends were measured as these brines are most commonly combined for additional benefits in the field. Although not completely linear in **Figure 3.2**, taking into account the measuring error, we can assume that viscosity of a Cs/K formate brine blend forms a linear relationship between the caesium and potassium formate standard (or stock) brines (2.20 g/cm^3 and 1.57 g/cm^3).

It is essential to measure the base brine viscosities, in order to evaluate a polymers full efficacy in solution. This is done by subtracting the brines intrinsic viscosity from the viscosity of the polymer solution to analyse degradation characteristics comparing viscosified brines when exposed to high temperatures. The importance of establishing Newtonian viscosities will become more apparent in later sections.

3.2 Compatibility of Common Biopolymers with Formate Brines

3.2.1 Compatibility of Biopolymers with Cs/K formate brine

From the literature, a number of common high molecular weight polysaccharides are stated as being compatible with highly concentrated formate brines for example; xanthan, scleroglucan and guar gum along with a few others – see **Table 3.1** and **Figure 3.3** (Howard 2009). Many of these experience a melting temperature (T_m) in solution which corresponds to an order-disorder transitional phase leading to a mass decline in viscosity. In addition, all of the polysaccharides listed below embody the same polymer backbone as xanthan gum; a tetrasaccharide repeating sequence. However, the variation of physical properties in solution arises from the presence of different side chains or functional groups (Member and Morris 1995).

Table 3.1 Common Polysaccharides and their Properties

Biopolymers	**Tradename/ Manufacturer**	**Ionic Charge**	**Arrangement in Solution**	**Molecular Weight (g/mol)**
Xanthan Gum	Xanvis/CP Kelco	Anionic	Branched	2.0×10^6
Welan Gum	BIOZAN/M-I SWACO	Anionic	Branched	6.6×10^5
Scleroglucan Gum	Actigum C6/Cargill	Non-ionic	Linear	4.0×10^6
Guar Gum	Sigma-Aldrich	Non-ionic	Linear	2.7×10^6
Carboxymethyl Guar Gum	BioAdd 830/Shrieve	Anionic	Branched	1.8×10^6

Figure 3.3 *Dry polymeric materials before addition to solution (photograph taken in CSF Laboratory)*

To evaluate the extent of these compatibilities in highly concentrated formate brines; temperature vs. viscosity profiles were measured for each biopolymer at 8.57g/L concentration in 2.0g/cm^3 Cs/K formate brine (pH 10.17, 8.57g/L K_2CO_3, 4.57g/L $KHCO_3$ buffer) using the Haake MARS III rheometer pressure cell @ 500s^{-1} shear rate.

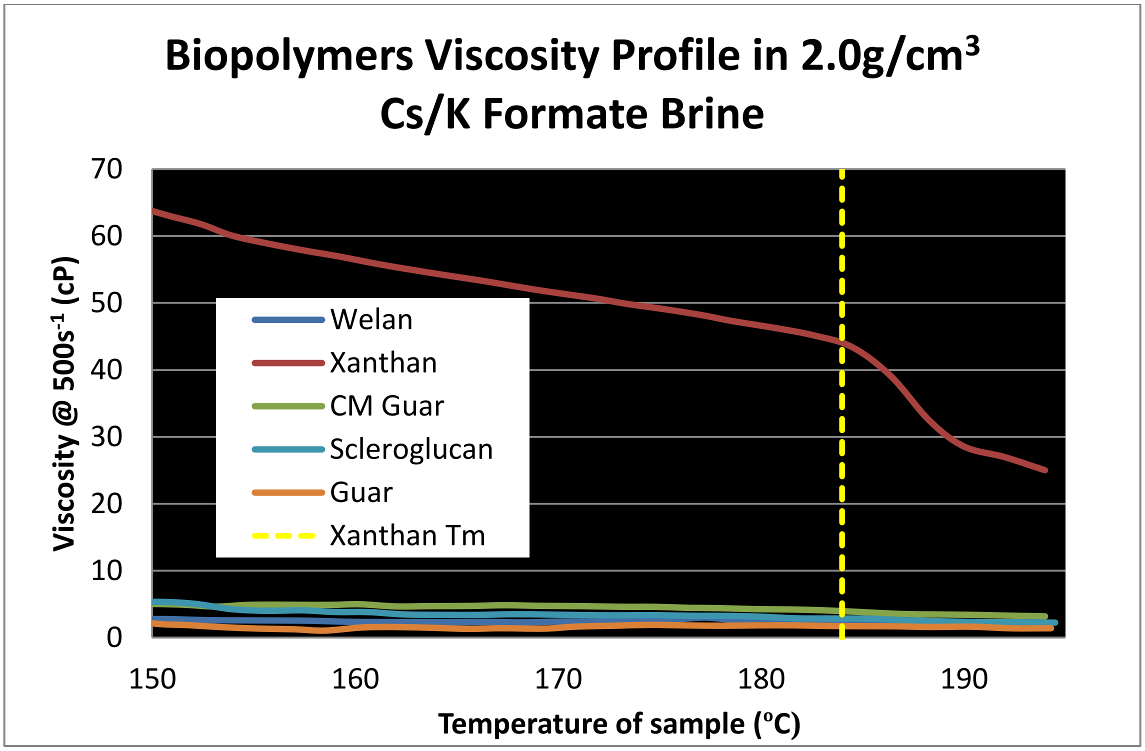


Figure 3.4 *Viscosity temperature profiles of various polysaccharides in buffered 2.0g/cm^3 Cs/K formate brine, pH 10*

Unfortunately, xanthan gum was the only biopolymer to demonstrate excellent thickening capacity at 8.57g/L concentration in 2.0g/cm^3 Cs/K formate brine, whereas the other polysaccharides provided little more viscosity than the Newtonian brine (6cP @ 50ºC) indicating they were unable to yield accordingly in the high salt concentrated solution. Xanthan's T_m is clearly visible from **Figure 3.4**, however the other biopolymers transition temperatures were either non-existent or too difficult to accurately measure in 2.0g/cm^3 C/K Formate stock brine. This is surprising as, in contradiction to previous publications (Howard 2009; Gallino et al. 1996) results have so far illustrated that highly concentrated buffered formate brines at pH 10 are incompatible with welan, scleroglucan, guar, and carboxymethylated (CM) guar, though seem to be extremely effective with xanthan gum – which will be discussed in more detail in section **3.3**.

3.2.2 Compatibilities of Biopolymers in Water

Since most of the respective biopolymers failed to hydrate in a standard 2.0g/cm^3 Cs/K formate brine, temperature viscosity profiles of each polysaccharide (at 8.57g/L) were re-measured in de-ionized water (brine + biopolymer ranged between pH 6-8) to compare properties.

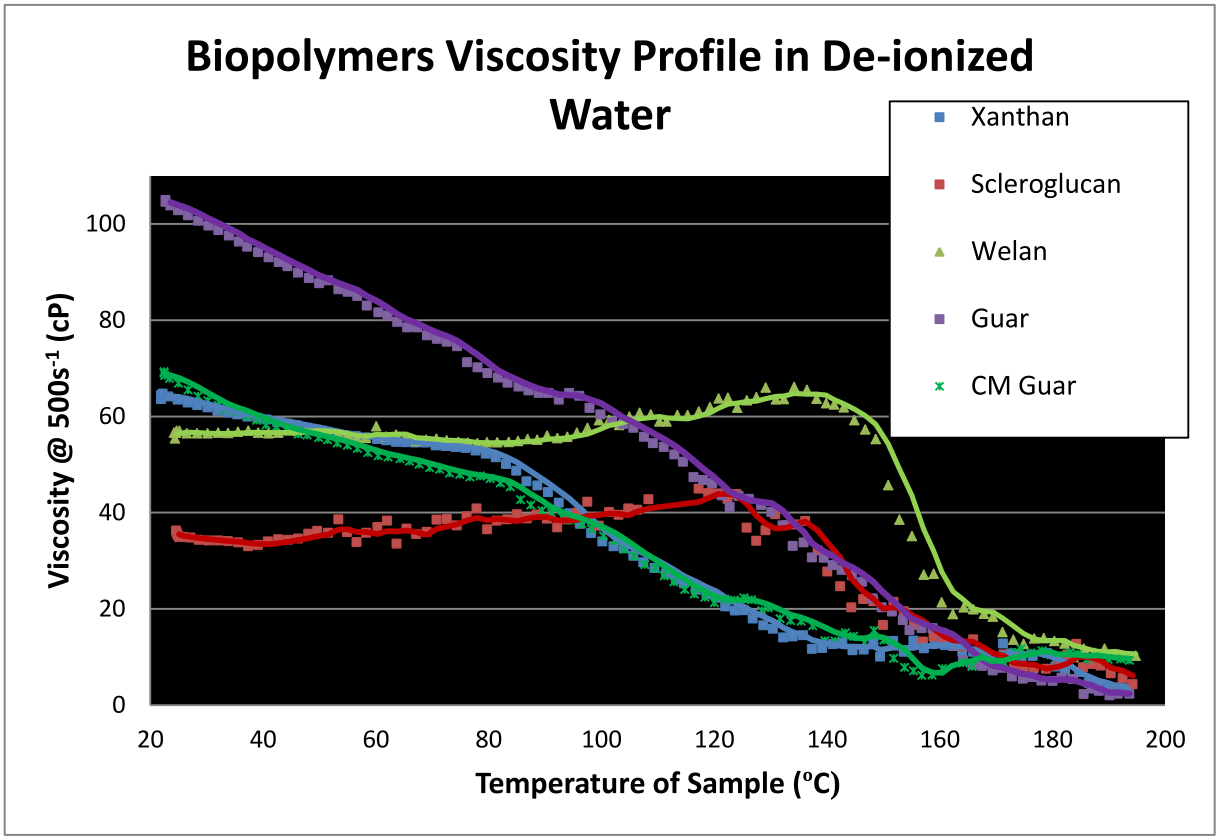


Figure 3.5 *Temperature viscosity profiles of various polysaccharides in de-ionized water, pH 6-8*

According to **Figure 3.5**, most of the biopolymers hydrate in water to demonstrate a clear order-disorder transitional change upon further heating, with the exception of the guar products (biopolymer T_m values recorded in section **3.2.4**, **Table 3.2**). So either the highly saturated formate salt solutions at 2.0g/cm^3 have insufficient free water (A_w = 0.29 @ 25ºC) for these polysaccharides to be able to hydrate, or the high pH and/or buffer content is inhibiting the hydration process.

3.2.3 The pH Effect on Biopolymers in Formate Brines

To counter-act the pH variable, solutions of the same brine; 2.0g/cm^3 Cs/K formate and 8.57g/L biopolymer were prepared with the buffer removed and pH lowered to around 7. Further temperature viscosity profiles were measured in order to compare physical characteristics of each biopolymer at the lower pH.

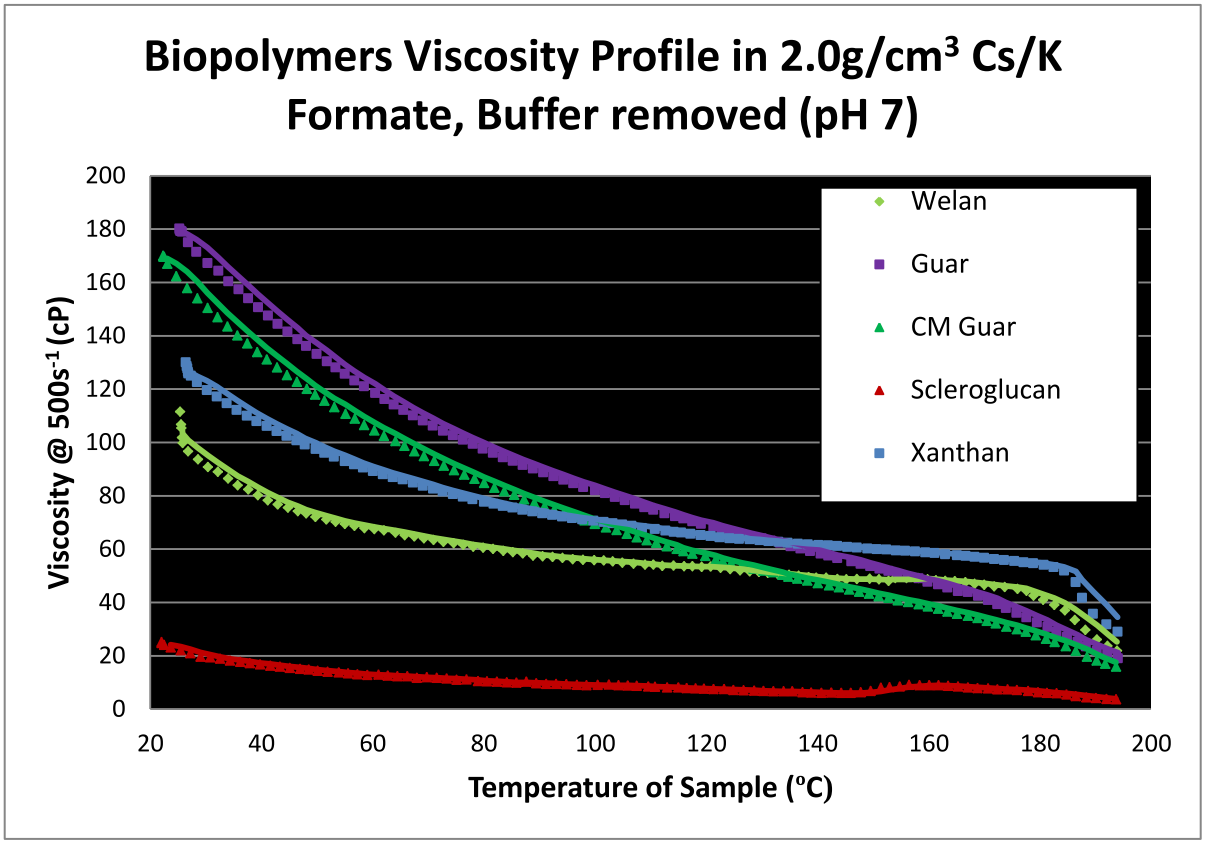


Figure 3.6 *Temperature viscosity plot of various polysaccharides in 2.0g/cm^3 Cs/K formate (buffer removed, pH 7)*

Results from **Figures 3.5 & 3.6**, highlight massive discrepancies with regards to hydration in water and in 2.0g/cm^3 Cs/K formate brine. As observed in section **3.2.1**, slightly buffered "13.1g/L carbonate/bicarbonate" brine at pH 10 does not hydrate the biopolymers (with the exception of xanthan gum), whereas removing the buffer content and lowering pH in most cases produces a far thicker solution than even it's pure aqueous phase. Results are in agreement with Wever *et al*, 2011 who implied that salts which are able to induce the structuring of water molecules (i.e. the formate anion) will lead to an increased viscosity due to the increased number of hydrophobic interactions (Wever, Picchioni and Broekhuis 2011). Also, enhanced T_m transitions in xanthan and welan gum can be observed in the low pH formate solution. Thus, contrary to popular belief; high salt concentration and insufficient free water is not the reason behind the hydration difficulties of polysaccharides in high density formate brines, but instead it is the high pH concern. Further, it is evident from **Figure 3.6**, that the high concentration of formate salt in solution is favouring the rigid ordered form of the polysaccharides backbone as the rheology profiles are relatively flat with increasing temperature in comparison to water.

Fann35 rheologies were recorded at 50ºC to compare viscosities of the biopolymers in water and in Cs/K formate brine.

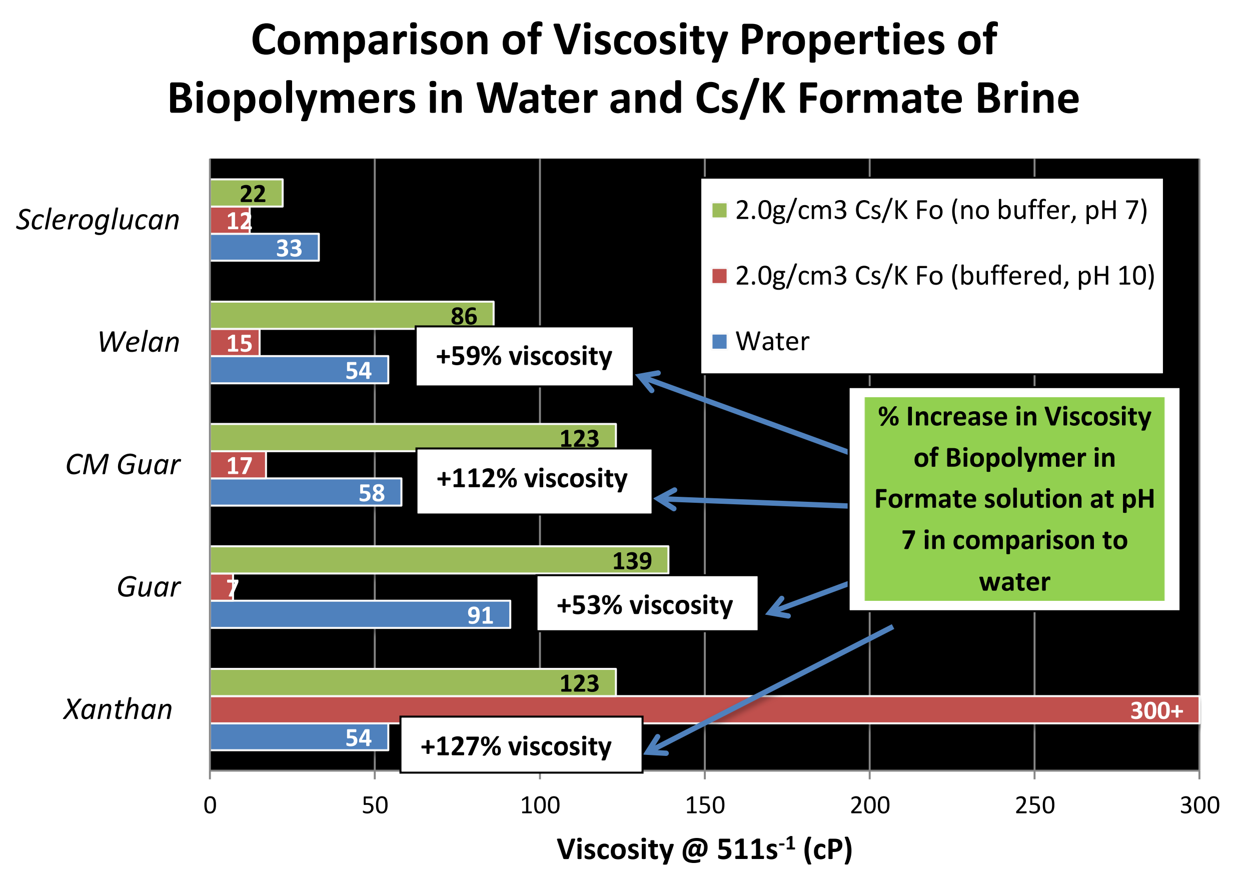


Figure 3.7 *Viscosities of each biopolymer (8.57g/L) in the various solutes at 511s^{-1} shear rate (Fann35) (Newtonian brine viscosity is 6cP @ 50ºC)*

Fann35 viscosity measurements @ 511s^{-1} (or 300rpm) are in close agreement with MARS III pressure cell profiles (**Figures 3.4, 3.5 & 3.6**), confirming that the results are accurate. Altering the pH of the solution disturbs the overall charge density of anionic polymers, and therefore influences electrostatic interactions in solution (Norton, Spyropoulos and Cox 2010). More specifically, decreasing the pH of a polymer solution normally enhances viscosity because of an increase in the polymer's hydrodynamic volume due to the protonation of carboxyl functional groups (Wever, Picchioni and Broekhuis 2011). However, this is only completely true in aqueous and semi-dilute environments so the addition of a large amount of salt can alter solution viscosity dramatically, even with the same concentration of biopolymer.

Polymer solution behaviour in high density formate brines is not well understood, as it has never been studied in any great detail before now. Therefore, it is especially interesting to discover that at neutral pH, biopolymers exhibit higher viscosities in concentrated formates than in pure aqueous solution (see **Figures 3.5, 3.6 & 3.7**). It has been well documented that in lower saturated brines, the effect of the salt screens the counter ion charges on the polyelectrolyte which would normally produce electrostatic repulsive interactions to stretch and elongate the polymer chain in aqueous solution (Moreno 2011). Since the polymer chains can no longer repel one other to the same degree as in water, the decrease in electrostatic associations causes a marked reduction in solution viscosity. However, Wyatt *et al*. 2011 suggested that if the concentration of monovalent salt ions exceeds the number of free counter ions available in the polymer solution (described as the "high salt limit"), then electrostatic interactions are predicted to be negligible and the polymer functions as neutral or non-ionic.

After the "high salt limit" has been attained in a solution with enough biopolymer to meet its critical concentration for cross-linking entanglement, an increase in viscosity is observed in monovalent sodium chloride brine instead of the expected decrease due to suppression of electrostatic associations. This is believed to be caused by increased hydrogen bonding as the lack of interchain repulsions allow the polymer chains to come into much closer contact and promotes strong intramolecular interactions in the form of hydrogen bonds. The significant increase in hydrogen bonding surpasses the influence of electrostatic associations between counter ions and effectuates an even higher solution viscosity because it is more difficult for chains to move past each other without interacting to form a more rigid network structure (Wyatt, Gunther and Liberatore 2011). Since Cs/K formate salt is far more soluble in water than sodium chloride, it will most definitely exceed the "high salt limit" at 2.0g/cm^3 (i.e. number of ions in solution is higher than the number of polymer counter-ions) required to enhance viscosity by enforced hydrogen bonding, so results are consistent with Wyatt *et al.* 2011 at neutral pH (see **Figure 3.8**). The effect of pH on polymers will be discussed further in sections **3.2.5** and **3.3.7**.

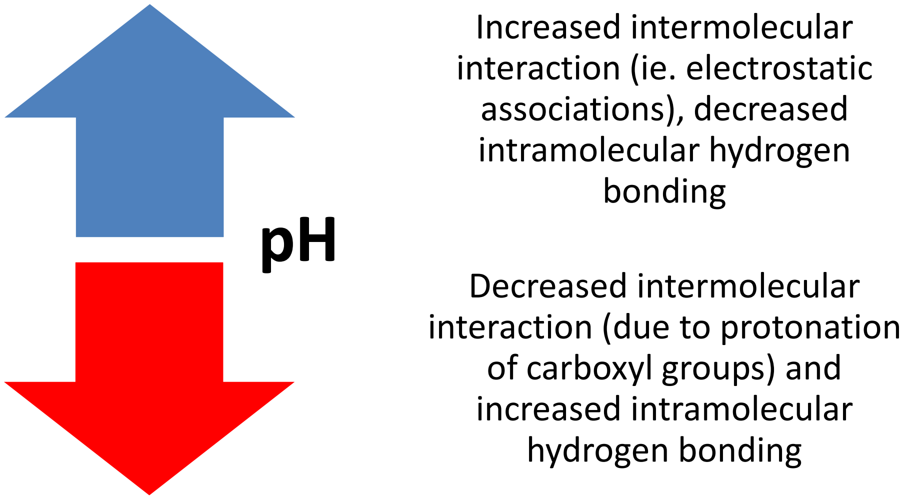


Figure 3.8 *General behaviour of biopolymers in aqueous solution with increasing/decreasing pH*

3.2.4 Stability of Biopolymers in Formate Brines

***Refer to section 2.1.9 & 2.1.10 to measure $T_{50\%}$ and T_m values**

It is well-known that alkali metal formate brines increase the temperature stability of biopolymers to withstand greater temperatures than in standard oilfield brines due to their unique ability to solubilize to extremely high concentrations in water (Howard 1995; Downs 1991). One measure of stability is the polymers T_m, or melting temperature where the molecule undergoes an order-disorder transition in which a clear drop in viscosity is observed. However, only certain biopolymers possess a T_m; so another measure of stability is to monitor the temperature at which the polymer solution experiences 50% viscosity loss ($T_{50\%}$) using MARS III Rheometer data.

Table 3.2 Measured T_m and $T_{50\%}$ of various biopolymers in water and 2.0g/cm^3 Cs/K formate, in buffered and unbuffered solutions

Biopolymers	**T_m in Water (°C)**		**T_m in 2.0g/cm^3 CsK Formate (°C)*** **Buffered, high pH**		**T_m in 2.0g/cm^3 CsK Formate (°C)*^{2}** **Unbuffered low pH**	
	T_m	**$T_{50\%}$**	**T_m**	**$T_{50\%}$**	**T_m**	**$T_{50\%}$**
Xanthan Gum	80	112	184	~~124~~	186	187
Welan Gum	150	160	NA	~~108~~	180	186
Scleroglucan Gum	137	156	NA	~~153~~	NA	118
Guar Gum	NA	123	NA	~~146~~	NA	124
Carboxymethyl Guar Gum	NA	112	NA	~~138~~	NA	116

***T_m in 2.0g/cm^3 Cs/K formate using lab stock, i.e. total buffer 13.1g/L $K_2CO_3/KHCO_3$ at pH 10.17**

***^{2}T_m in 2.0g/cm^3 Cs/K formate with buffer removed, and pH lowered to around 6-7 in the brine.**

The $T_{50\%}$ in buffered 2.0g/cm^3 Cs/K formate highlighted in **green** are not a good representation of stabilizing potential, as initial viscosities were so low due to lack of polymer hydration (see **Figure 3.4**), therefore it could be misleading as to draw conclusions from their measured $T_{50\%}$ values. However, the unbuffered 2.0g/cm^3 Cs/K formate results provide clear answers with regards to T_m and $T_{50\%}$ and will be used to quantify the significance of using Cs/K formate salts to protect the various biopolymers in comparison to water (**Figures 3.9 & 3.10**).

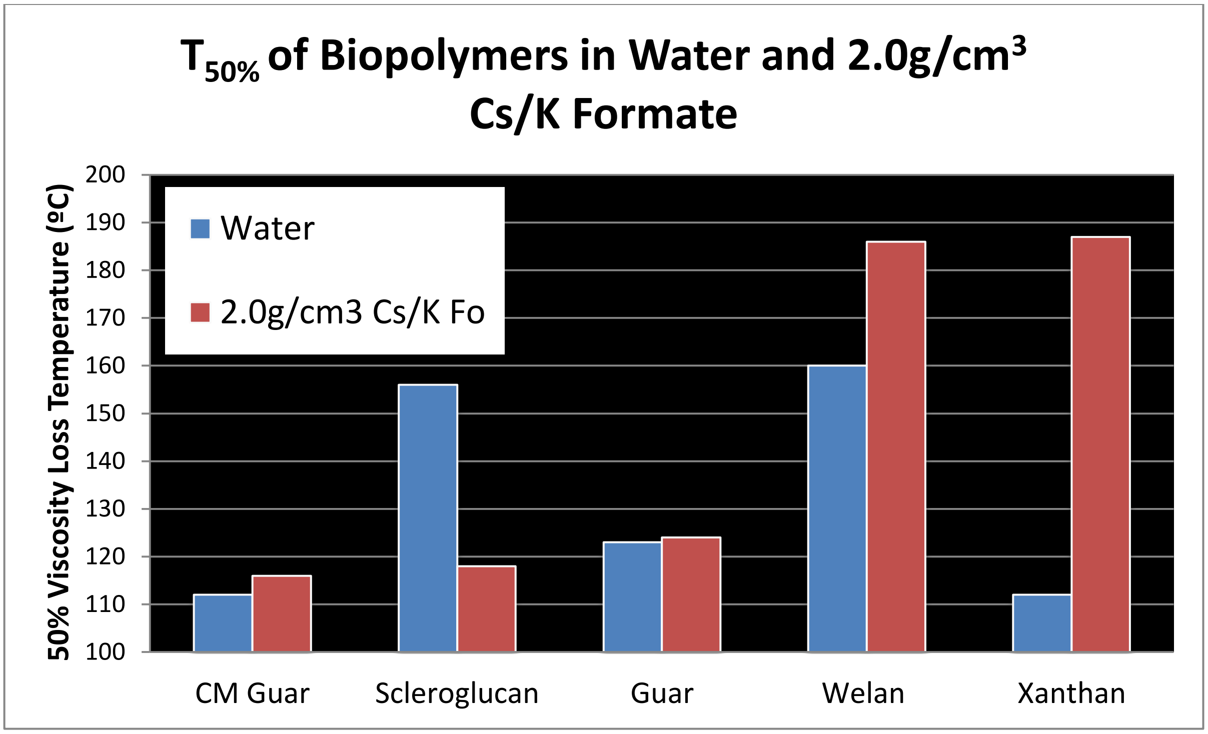


Figure 3.9 *Differences in $T_{50\%}$ of 8.57g/L biopolymer in water and 2.0g/cm^3 Cs/K formate solution*

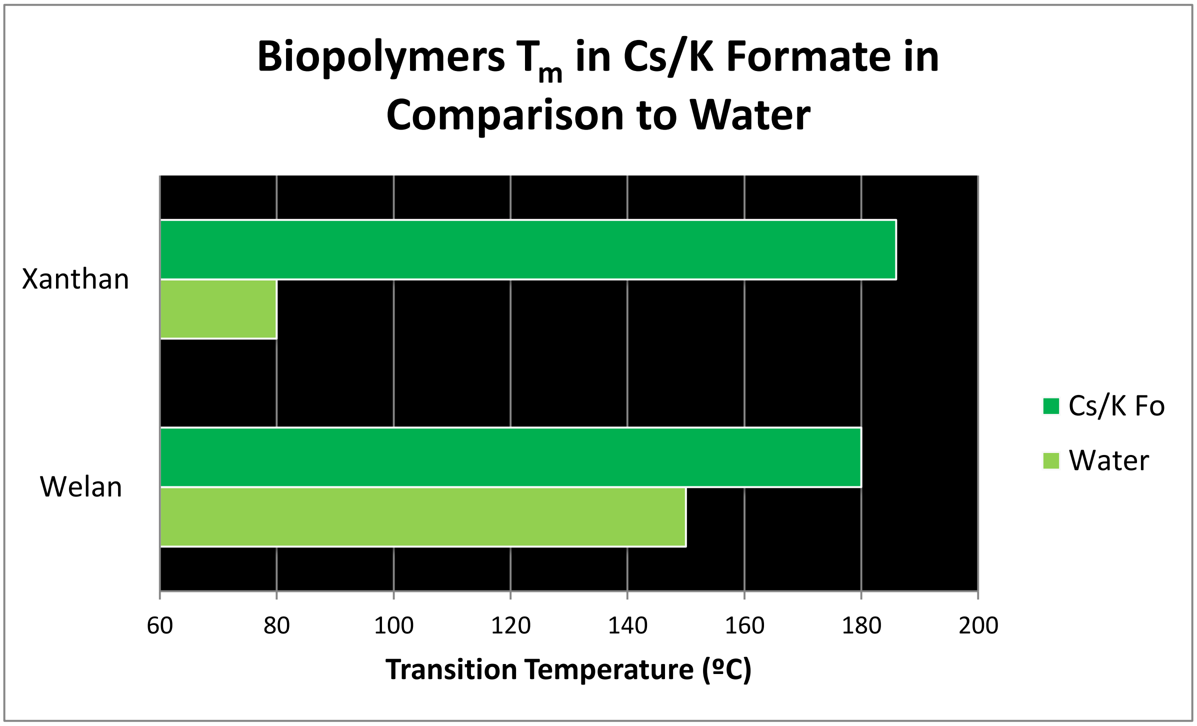


Figure 3.10 *Increase in T_m of xanthan and welan gum (8.57g/L) in 2.0g/cm^3 Cs/K formate in comparison to de-ionised water*

With respect to increasing the temperature stability of biopolymers, results have demonstrated that Cs/K formate brine at 2.0g/cm^3 can enhance the T_m and $T_{50\%}$ of various polysaccharides when allowed to hydrate properly; the most significant increases were observed in xanthan and welan gum (**Figure 3.10**). With that said, scleroglucan seems unable to hydrate in this particular blend of Formate under any pH condition, and perhaps would be more suitable for use in less concentrated brines, given its high T_m in water.

From the literature, scleroglucan is acknowledged to remain insensitive to salinity and mechanical degradation because of its non-ionic functionality, and triple helix semi-rigid structure which can increase temperature resistance compared to other similar polysaccharides (Kulawardana et al. 2012). However, Glass *et al*, 1983 recognized that alkalinity disrupts the hydrogen bonding that promotes the stable helical formation of scleroglucan in solution – much like urea does for xanthan gum (Glass et al. 1983). Results from the current study have confirmed that scleroglucan or "Actigum C6" is incompatible with concentrated Cs/K formate brine (2.0g/cm^3) at any pH. Adversely, an earlier review described scleroglucan as having excellent viscosifying capabilities in potassium formate brine - but only in solutions up to 40 g/L; so in essence, it may only be compatible in extremely low formate concentrations (Gallino et al. 1996).

The biopolymer welan gum has not been previously investigated for use in formates and therefore an increased T_m measurement of 180ºC (30ºC higher than in water) is intriguing as it could potentially compete as an alternative viscosifier to xanthan gum if a new method of polymer hydration at higher pH is discovered. At neutral pH, intra chain hydrogen bonding is increased significantly due to lack of "free space" in Cs/K formate solution caused by the high concentration of salt - even though electrostatic interactions on the polymers carboxyl group may be screened and the polymer chain cannot elongate (Wyatt, Gunther and Liberatore 2011). This salt induced configuration and increased hydrogen bonding is predicted to be the main reason for the increase in T_m of anionic welan gum in 2.0g/cm^3 Cs/K formate, as it promotes further chain rigidity and reduces exposure of radical susceptible sites which can induce degradation.

Guar gum and it's modified derivative; carboxymethyl guar were compatible and provided a good measure of viscosity at neutral pH but did not exhibit a clear order-disorder transition temperature when heated in Cs/K formate or aqueous solution - though, there was no mention of guar gum having a T_m in any of the subsequent literature studies. Another interesting observation is that non-ionic standard guar gum produces a thicker fluid than CM guar in both 2.0g/cm^3 Cs/K formate as well as in water which is in slight disagreement to the literature. Authors, Lei and Clark have discussed carboxymethylated polymers (such as CM guar) and how their negatively charged groups repel causing the molecules to occupy a larger volume, leading to increased viscosity from that of its neutral state; for example in non-ionic standard guar (Lei and Clark 2004). However, since the high concentration of formate salt at 2.0g/cm^3 should exceed the "high salt limit" and negate electrostatic effects of the counter ions, the solution maintains charge neutrality so viscosity will build as a result of increased intramolecular hydrogen bonding (Wyatt, Gunther and Liberatore 2011). Therefore, CM guar loses its slight ionic charge, so the larger molecular weight of the standard guar (33% higher) is predicted to be the reason for enhanced viscosity over its carboxymethyl modified derivative in this instance.

Further, an important point worth mentioning is that a 2.0g/cm^3 Cs/K formate is not the best choice of brine for stabilizing polymers as the majority of it is prepared from caesium formate stock, whereas if saturated potassium formate alone had been used as the base fluid; there would be larger increases in stability margins certainly with regards to xanthan and welan gum (see section **3.3.3**). Similarly, the more potassium added to the standard Cs/K formate blend (i.e. for the lower densities between 1.57-2.20g/cm^3), the higher the temperature stability of polymer (see section **3.3.4**). Therefore, since the 2.0g/cm^3 Cs/K formate has been employed on this occasion as a "standard" to solely compare the variable biopolymer, it is worth bearing in mind that these limits can be extended by simple engineering of the formate base brine.

Although most of the biopolymers managed to hydrate in 2.0g/cm^3 Cs/K formate at neutral pH, it is not practical to remove the buffer and lower pH for field applications as the carbonate/bicarbonate buffer package is essential to combat influxes of acid gas (Howard and Downs 2009). Therefore, an alternative solution must be established in order to ensure these biopolymers function efficiently in buffered formate brines with pH above 9.5.

3.2.5 Alternative Hydration Methods for Biopolymers in Cs/K formate Brine

***Refer to section 2.1.10 to measure T_m values**

- **Adding Biopolymers in Liquid Form**

For ease of use and to improve dispersion, many polymers are applied in liquid form, normally pre-mixed into glycol or another solvent. Therefore, since welan gum is known to be soluble in polar organic solvents such as ethylene glycol (Member and Morris 1995), it was used as a precursor to hydrate the welan before adding to buffered 2.0g/cm^3 Cs/K formate, pH 10 at 8.57% by volume (20g welan in 200mL MEG) as equivalent to 8.57g/L powder to compare with previous tests.

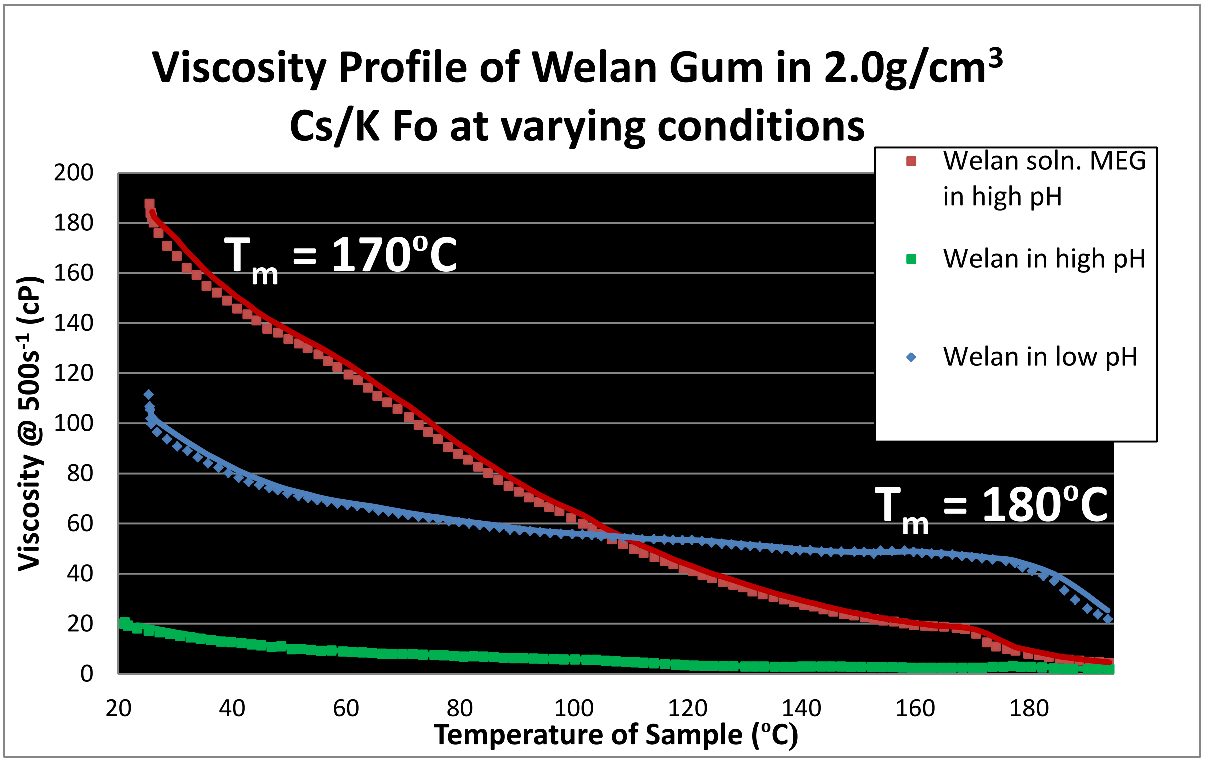


Figure 3.11 *Temperature viscosity profiles of 8.57g/L welan gum administered to 2.0g/cm^3 Cs/K formate in powdered form and ethylene glycol*

Consequently, administering welan in liquid glycol to 2.0g/cm^3 Cs/K formate ("Welan soln. MEG in high pH") is a vast improvement with regards to hydration than its powdered form in the same brine ("Welan in high pH"). However, **Figure 3.11** illustrates that it's still not as effective as in unbuffered Cs/K formate ("Welan in low pH") at higher temperatures, as viscosity is around 100% lower >160ºC and T_m drops by 10ºC. This makes sense as the glycol MEG addition was 8.57% of the total volume, therefore reducing the amount of formate salt available to protect the polymer backbone – so glycosidic polymer linkages will be more exposed for chemical attack. These findings again, re-iterate the importance of maintaining a high concentration of formate salt in solution.

- **Applying Heat to Hydrate Polymers**

Occasionally, polymers require a certain amount of heat energy in order to "swell" and enhance their solution viscosities, especially in saturated brines. After gentle heating, the polymers functional groups are more easily accessible for intermolecular association – causing their influence in solution to intensify (Renou et al. 2013). Therefore, to evaluate if the biopolymers hydrate after heating in buffered 2.0g/cm^3 Cs/K formate; the fluids (omitting xanthan as it is compatible anyway) were dynamically aged for 16 hours at 120ºC and their Fann35 viscosities were recorded @ 511s^{-1} (cP). The temperature of 120ºC was selected as it is unlikely that any of the polymers would degrade over 16 hours in such concentrated brine so the resultant viscosity should solely provide answers about the molecular conformation of the polymer, rather than any potential stability concerns.

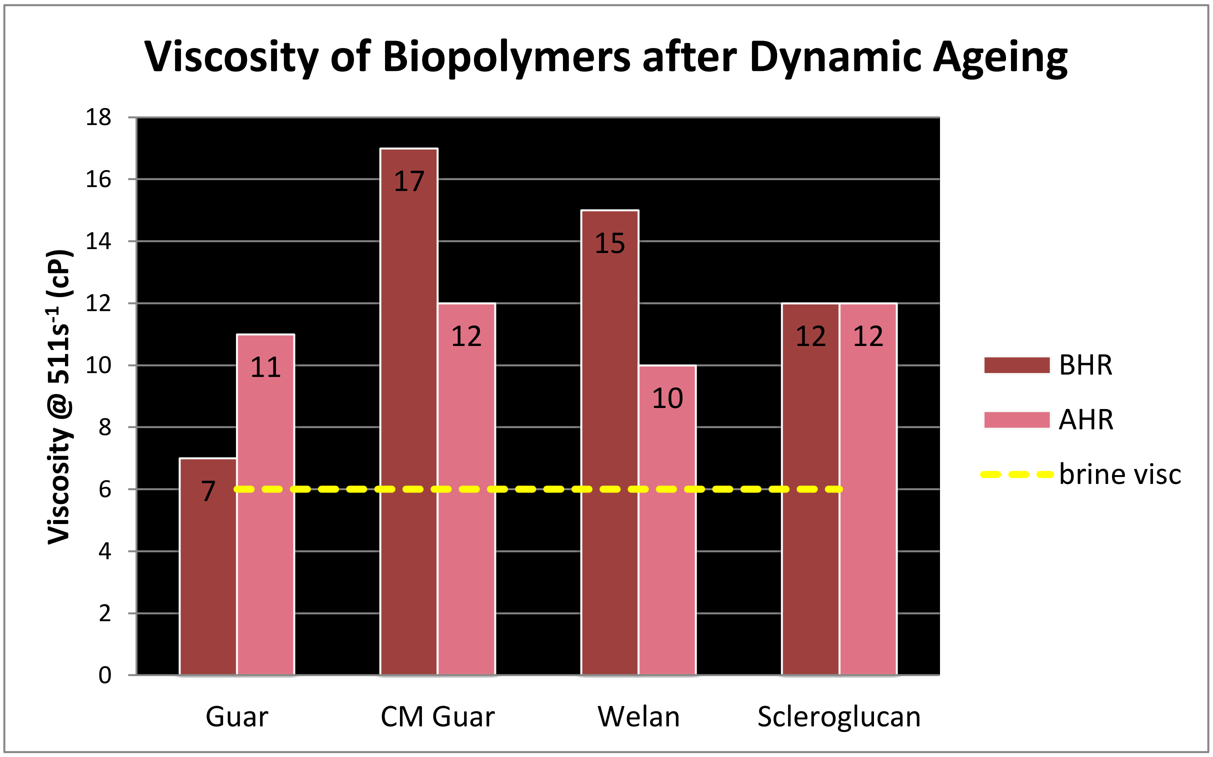


Figure 3.12 *Fann35 viscosities of 8.57g/L biopolymers in buffered 2.0g/cm^3 Cs/K formate (pH 10) before and after heating for 16 hours @ 120ºC*

Unfortunately, **Figure 3.12** demonstrates that dynamic ageing @ 120ºC does not improve hydration of biopolymers in buffered Cs/K formate, and therefore it seems more likely that manipulation of pH/buffer is inevitable in order to "activate" the guar's, welan and scleroglucan gum in 2.0g/cm^3 Cs/K formate brine. Luckily, the most widely used polysaccharide in formate drilling fluids; xanthan gum does not have this same issue.

- **Hydrating Polymers in Low pH Cs/K formate Before Adding Buffer**

To investigate whether hydrating polymers in neutral 2.0g/cm^3 Cs/K formate and then adding buffer to increase pH would influence fluid viscosity; 13.1g/L potassium carbonate was added to low pH pre-hydrated polymer Cs/K formate solution at 8.57g/L, to simulate the same content of buffer and a similar pH as the standard buffered Cs/K formate (pH 10) used in section **3.2.1**.

Interestingly, after potassium carbonate addition both guar products began to cross-link and aggregate immediately becoming very "elastic" – this is most likely due to the competing effects of electrostatic interactions (promoted by addition of buffer) and intramolecular hydrogen bonding (already present at the lower pH) between the polymer chains (Wyatt, Gunther and Liberatore 2011). However, after the sample was left on the bench for around an hour; the polymer visually began to precipitate out of solution; leaving a clear brine layer visible on the surface and surrounding the "gelled" guar with the dehydration effect becoming progressively worse over time (see **Figure 3.13**). A similar situation occurred with CM guar, although not quite as noticeable at first glance. This is particularly interesting, as during the CSF brine recycling process, high pH is employed to precipitate out polymers, such as guar or xanthan gum.

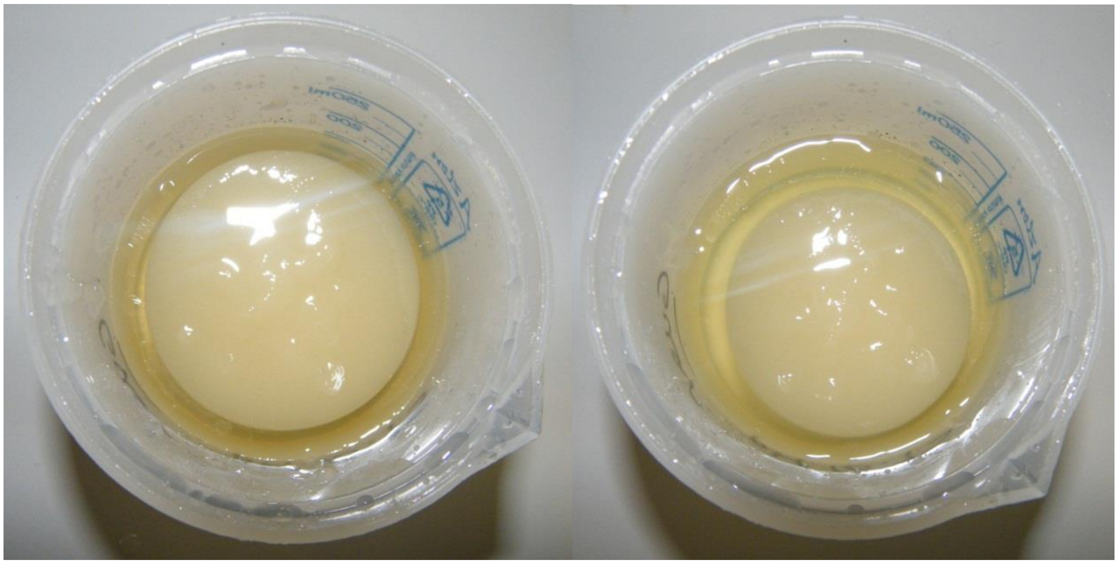


Figure 3.13 *Guar gum in 2.0g/cm^3 Cs/K formate, initially hydrated at low pH before adding 13.1g/L carbonate to simulate std. brine conditions, photographed after 1 hour (left) and then overnight (right)*

Soon after adding the buffer (and before the polymer began to precipitate), a sample was measured in the MARS III HPHT rheometer to evaluate its rheological profile.

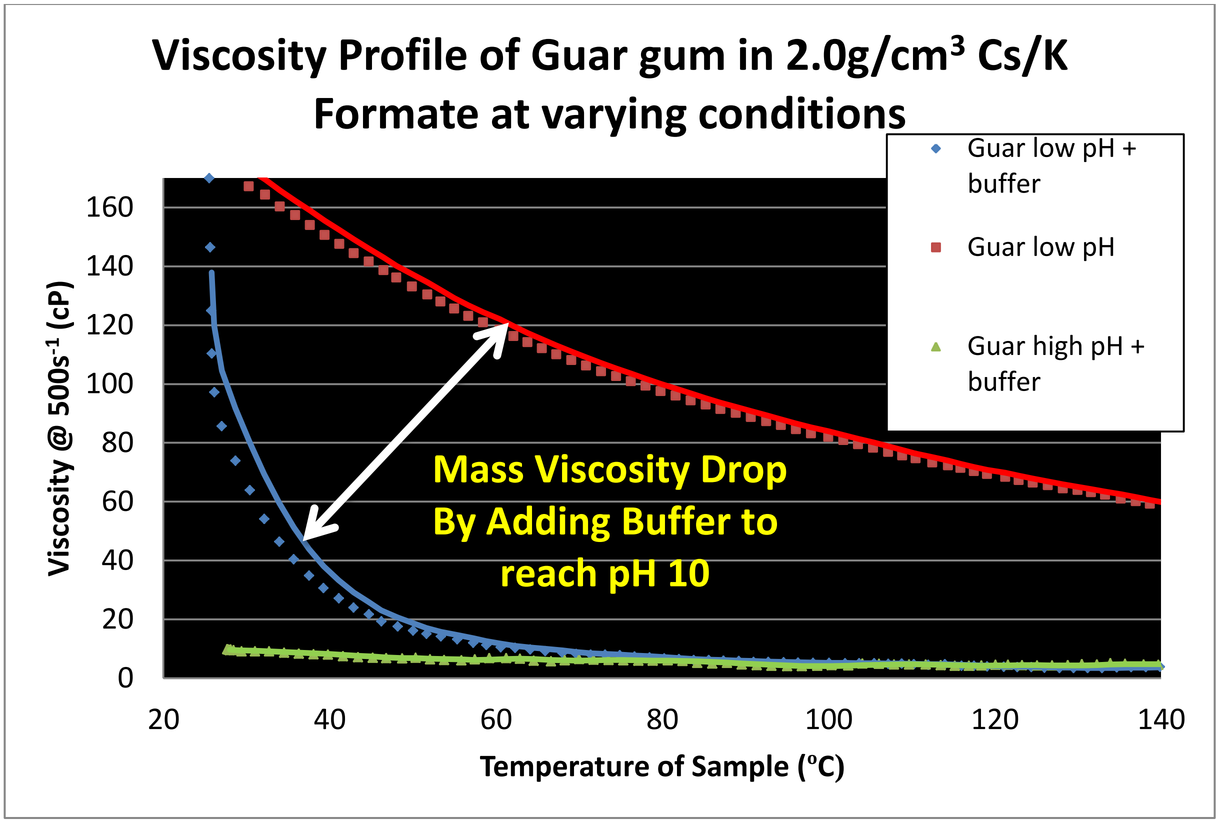


Figure 3.14 *Temperature viscosity profiles of 8.57g/L Guar gum administered to 2.0g/cm^3 Cs/K formate at varying pH and buffer content*

Figure 3.14 shows an exponential decrease in rheology after heating, and by 80ºC the guar solution viscosity had completely reverted back to its original state in buffered high pH brine ("Guar high pH + buffer"), and did not recover after cooling. The same rheological pattern was mirrored for CM guar, welan and scleroglucan; so the method of adding polymers at low pH and then using carbonate buffer to regain alkalinity completely reverses the hydration process.

Since the system is reversible, it is clear that the loss in viscosity is due to changes in molecular conformation rather than polymer degradation (García-Ochoa et al. 2000). Wever *et al*. 2012, states that the high ionization of carboxyl groups at pH 9 and above; favours intermolecular electrostatic interactions between the polymer molecules in aqueous solution. However, since guar gum is non-ionic; there should be very little electrostatic associations influencing rheology but the increase in pH will disrupt prevalent intramolecular forces (such as hydrogen bonding), which essentially controls viscosity in the absence of charges.

Therefore, the increase in pH caused by carbonate buffer addition, breaks the strong intramolecular network structure causing a mass decrease in viscosity as the polymer precipitates from solution (see **Figure 3.13**) (Wever, Picchioni and Broekhuis 2011). With regards to anionic biopolymers such as welan and CM guar; it has been suggested that the high concentration of monovalent salt in 2.0g/cm^3 Cs/K formate exceeds the "high salt limit" and neutralizes the electrostatic effects promoted by high pH. Therefore, results from this study have indicated that increasing pH has a similar effect for ionic polymers (apart from xanthan) as it does for neutral macromolecules in high concentrated brine systems like the formates (Wyatt, Gunther and Liberatore 2011). In this instance, more emphasis should perhaps be allocated to the average molecular weight of the biopolymer for viscosifying power, as the greater number of polymer chains forced closer together in a concentrated formate brine implement a stronger intramolecular network structure to improve solution viscosity (see **Figure 3.15**).

Order of Increasing Average Molecular Weight (g/mol) and Solution Viscosity (cP)

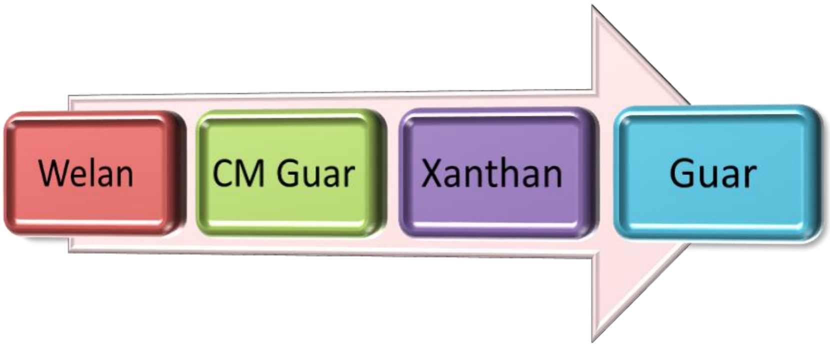


Figure 3.15 *Solution viscosity is enhanced in high concentrated formate brines at neutral pH with increasing molecular weight of biopolymer (interpreted from **Table 3.1 & Figure 3.6**)*

With that said, it is enlightening to see that in 2.0g/cm^3 buffered Cs/K formate, xanthan was the only biopolymer to hydrate better at high pH than at neutral. To investigate further, rheological profiles were measured of xanthan in unbuffered, 2.0g/cm^3 Cs/K formate at neutral pH with 13.1g/L carbonate, similar to **Figure 3.14** to see if this effect was also reversible.

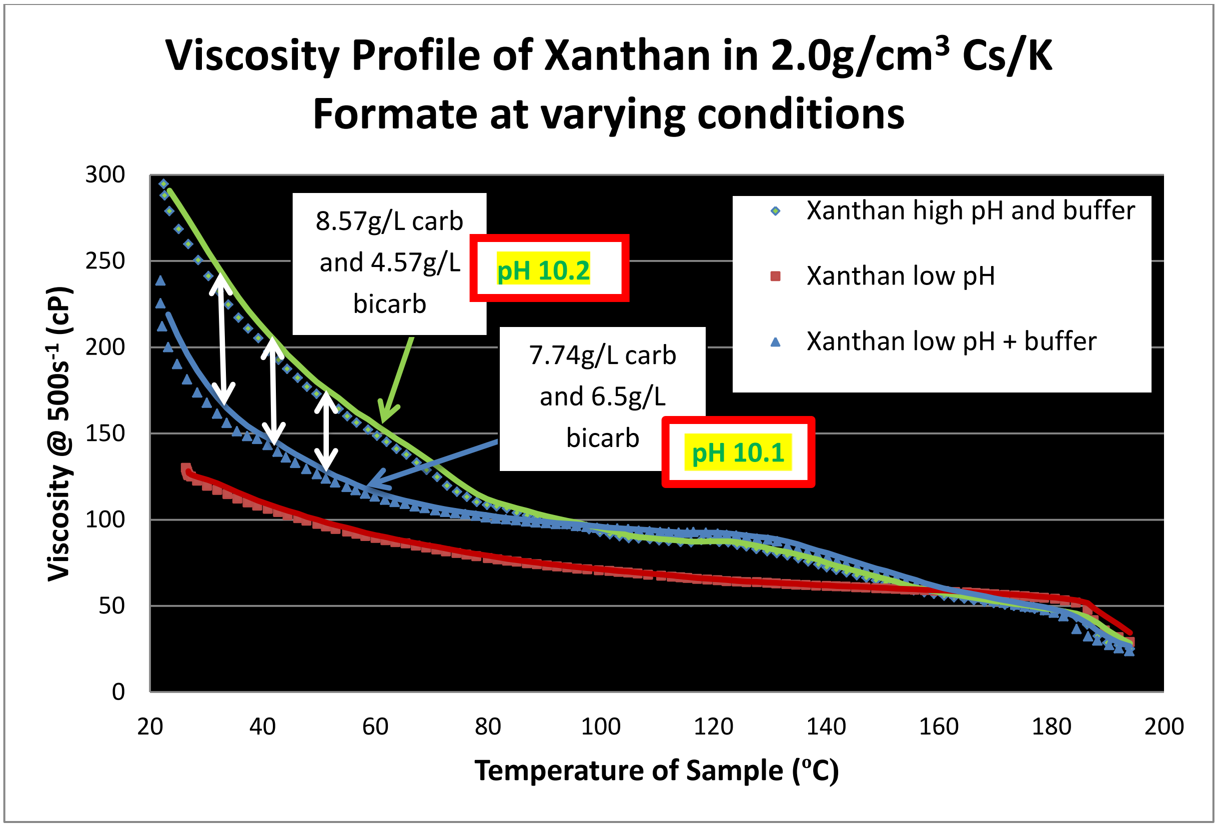


Figure 3.16 *Temperature viscosity profiles of 8.57g/L Xanthan gum administered to 2.0g/cm^3 Cs/K formate at varying pH and buffer content*

According to **Figure 3.16**; the effect is reversible above 100ºC, as it mirrors the original "Xanthan high pH + buffer" solution, however instead of decreasing its hydration (as observed with guar and other bio gums), the addition of buffer actually increases the viscosity of 2.0g/cm^3 Cs/K formate xanthan solutions. There are some differences in viscosity at the lower temperatures between the high pH Cs/K formate analogues so the effect is not completely reversible, which could be contributed to the slight variation of carbonate/bicarbonate in solution (see **Figure 3.16**). Another possible explanation could be; that "Xanthan low pH + buffer" was analysed around 10 minutes after the buffer was added (to "Xanthan low pH"), so the carbonate may not have had time to fully react and increase polymer entanglement at the lower temperatures.

Consequently, since xanthan gum has exhibited improved hydration properties at increasing pH where intermolecular electrostatic attractions are enhanced due to ionization of carboxyl groups ($COOH = COO^- + H^+$); this invalidates the concept that all biopolymers must behave as non-ionic in 2.0g/cm^3 Cs/K formate (Wyatt, Gunther and Liberatore 2011). Thus, xanthan gum must have some unique quality in comparison to other anionic biopolymers (i.e. CM guar, welan) which allows it to induce associations at high pH in concentrated formate brines – possibly through its large charge density and increased intermolecular hydrogen bonding through the terminal pyruvate ketal groups (indicated by optical rotation studies), which are not present in the other biopolymers (Auerbach 1985).

Results from section **3.2** and later in **3.3**, have highlighted significant irregularities with regards to xanthan's behaviour in the various formate brines through varying pH and buffer content. For example, the viscosity of single salt caesium formate with the same concentration of xanthan decreases with added buffer and elevated pH; whereas a 2.0g/cm^3 Cs/K formate blend with a small amount of potassium (32% stock brine or 41% in overall molar concentration) enhances viscosity by a factor of 5 (see **Figure 3.17**).

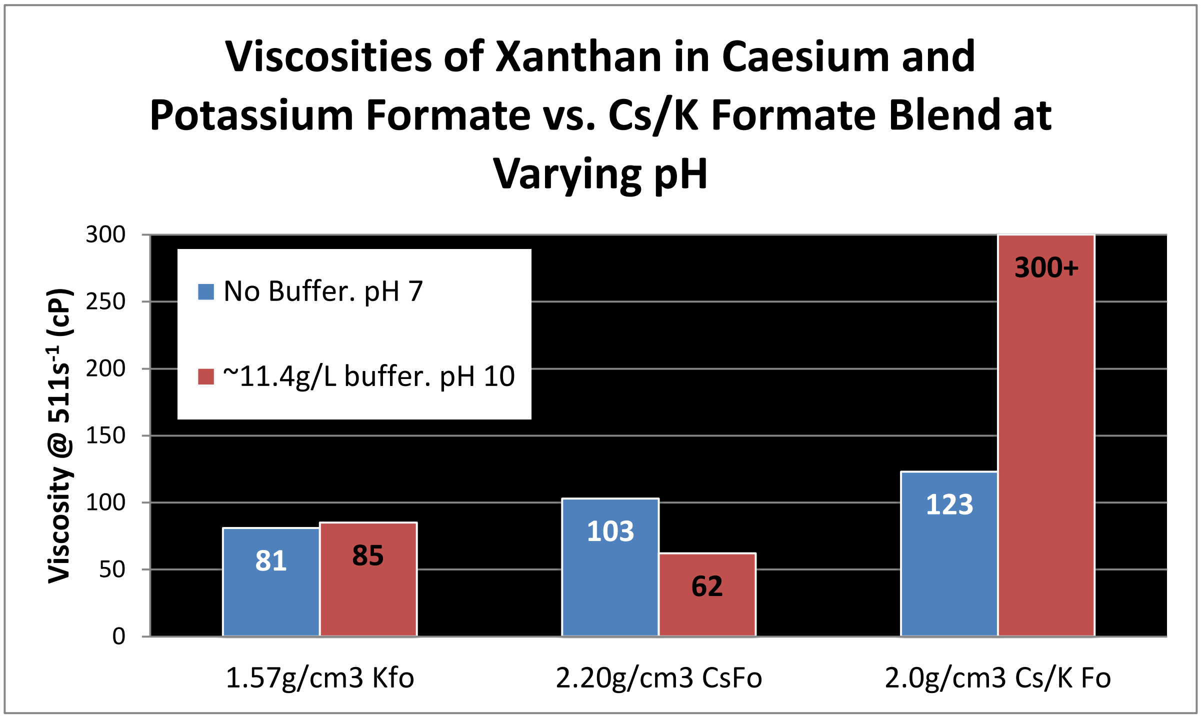


Figure 3.17 *Fann35 viscosities @ 50ºC of single salt caesium and potassium formate and a 2.0g/cm^3 standard blend before hot-rolling, buffered and non-buffered brine at varying pH*

Alternating the size and shape of the cation in salt solutions can affect polymeric solutions, although the effect is notably more pronounced in divalent brines rather in monovalent, according to the literature (Wyatt, Gunther and Liberatore 2011). In this instance, the larger cation caesium produces a higher viscosity at neutral pH with xanthan than potassium formate even though there are less molecules in solution - the same trend is observed when comparing caesium and potassium formate at similar salt concentrations (10.1mol/L) in section **3.3.5** (see **Figure 3.25**). However, adding potassium to caesium formate solutions apparently enables a less compact structure (Howard 2011a) where polymer chains may swell and extend due to influence of different sized molecules in solution and enhanced intermolecular associations at elevated pH - which could be responsible for the huge viscosity increase (see **Figure 3.17**; 2.0g/cm^3 Cs/K formate). The effect of pH and buffer in caesium and potassium formate with xanthan will be discussed further in section **3.3.7**.

Through knowledge gained from section **3.2**; after measuring biopolymer compatibilities in Cs/K formate brines it can be concluded that xanthan gum is the clear polysaccharide of choice in terms of temperature stability, viscosity effects and ease of use seeing as it does not need to be treated in order to hydrate in buffered formate brines. Therefore, considerable effort has been applied in the later sections to better understand the stabilizing properties with regards to xanthan gum in formates for application in extreme temperature environments.

3.3 Evaluation of the Effect of Xanthan Gum in Formate Brines

3.3.1 Qualification of Xanthan Products

Xanthan gum is one of the most commonly used biopolymers in the drilling fluids industry today, so many different grades and products are available which can subsequently vary in performance. In order to evaluate which grade of xanthan gum yields the best performance for high temperature application, a range of established products from various chemical and drilling fluid companies were analysed in a standard 2.0g/cm^3 buffered caesium/potassium formate brine (8.57g/L K_2CO_3, 4.57g/L $KHCO_3$) pH 10.

Table 3.3 Xanthan Products

Xanthan Trade Name®	**Company**
Xanvis	CP Kelco
Kelzan Advanced	CP Kelco
Flowzan	Drilling Specialties
Duotec	M-I SWACO
Flovis	M-I SWACO
Duovis	M-I SWACO

Arguably one of xanthan’s most valuable properties when used in a drilling fluid, is it’s highly shear thinning behaviour which can be illustrated by plotting shear rate vs. shear stress from Fann35 rheometer data (**Figure 3.18**).

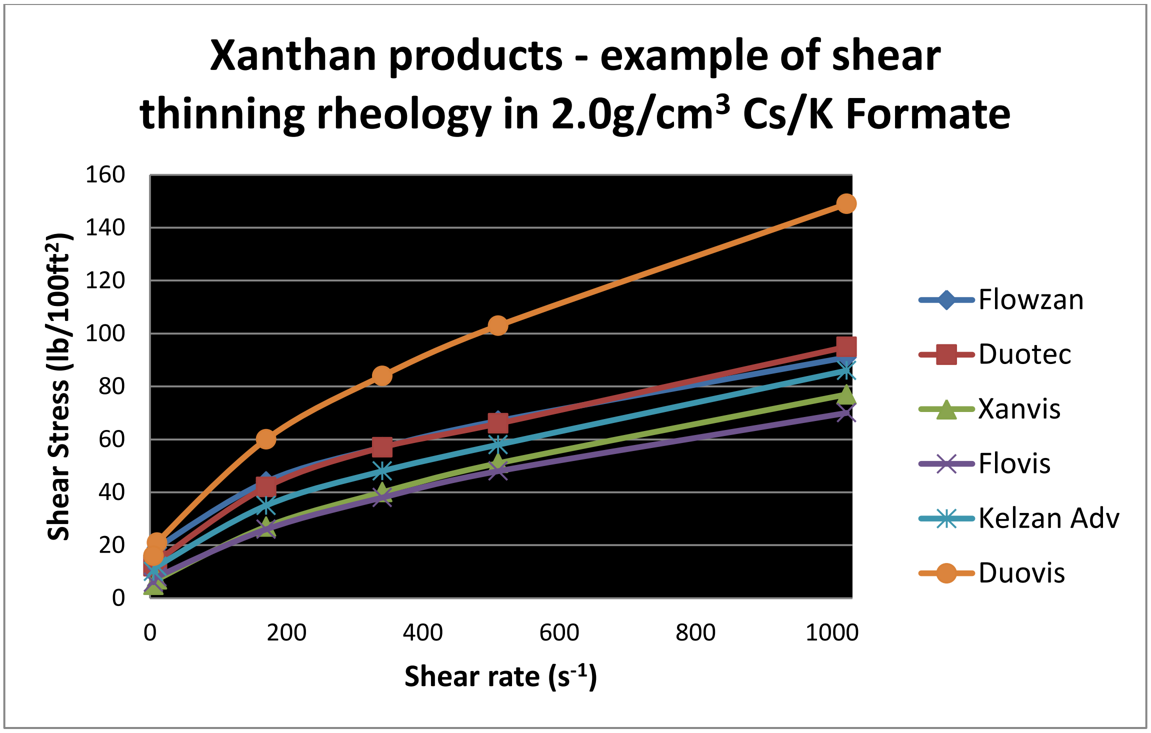


Figure 3.18 *Rheology measurements for each grade of xanthan (8.57g/L) before dynamic ageing*

As expected, all of the xanthan products demonstrate a non-Newtonian shear thinning rheological profile. However, altering the ratios of pyruvate and acetyl groups on xanthan's trisaccharide side chain can potentially affect stability along with other variation in positioning, length and composition of the trisaccharide chain (Downs 1991). Therefore, depending on fermentation and operating conditions, various xanthan products tend to exhibit different properties with regards to decomposition at high temperatures. To confirm this, each xanthan viscosified fluid was then hot-rolled for 16 hours at 150, 160, 170 and 180ºC and plotted in **Figure 3.19**.

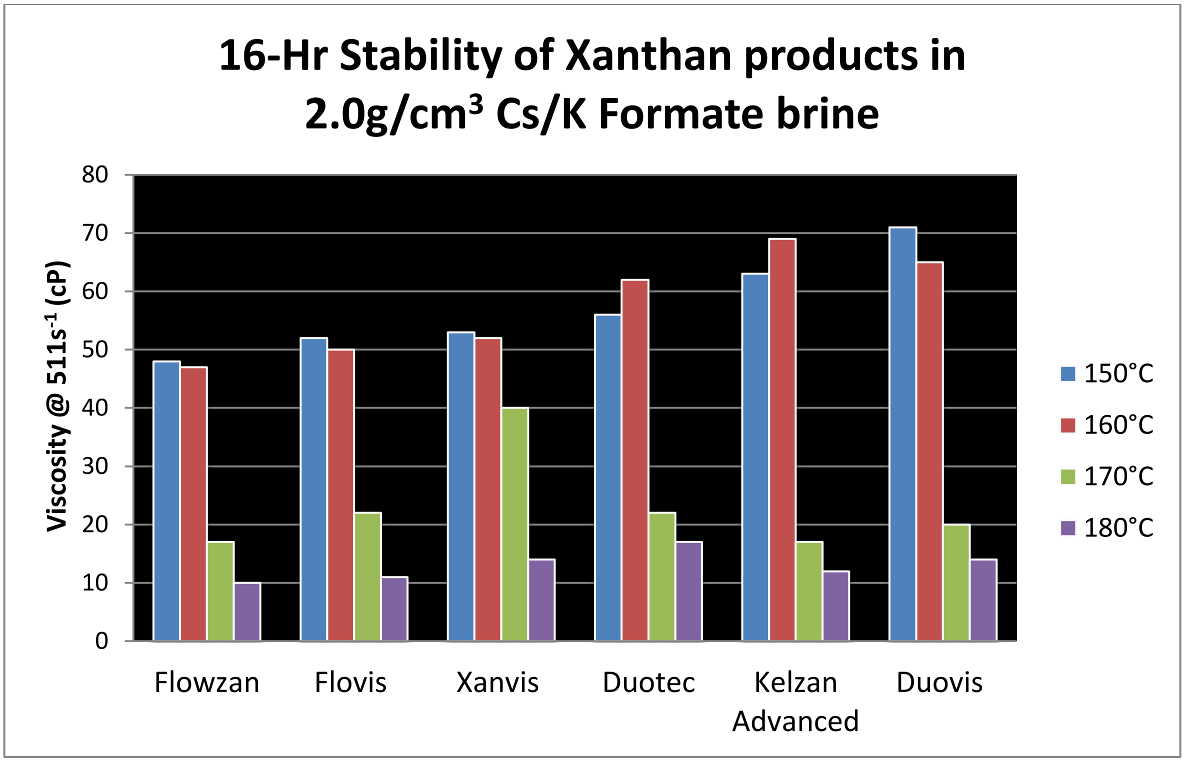


Figure 3.19 *Viscosity after 16-hr dynamic ageing of each xanthan product at the various temperatures*

In general, results from **Figure 3.19** demonstrate little discrepancy in product performance between the various brands of xanthan gum; however some grades do seem to maintain better resistance to degradation at higher temperatures than others. Considering the data and availability of each product, it was decided to use ***CP Kelco's Xanvis*** as the principle xanthan component for use in further experiments as it illustrates good overall stability in caesium/potassium formate brine.

3.3.2 Viscosity of Xanthan Gum in Formate Brines

With regards to viscosity, there is much uncertainty and limited literature studies applicable to explain xanthan gums behaviour in highly concentrated brines such as the formates, where there is much less water available for hydration. The behaviour of ionic polymers in salt brines is increasingly complex, as there are many factors such as chain orientation, chain stiffness, overlap, entanglement and electrostatic interactions which have to be taken into consideration when evaluating a polymers efficacy in solution (Wyatt, Gunther and Liberatore 2011). In the drilling fluids industry, a common misconception is that anionic polymers such as xanthan do not hydrate as well in saturated brines as they do in fresh water. The reasoning behind this is that; in salt solutions, the predominant metal cation (usually sodium) is suppressed or "pushed back" onto the polymer's functional group, thus increasing the distance between hydrated polymer molecules, which in turn causes the molecules to contract or coil and fluid viscosities to fall (Fink 2011; Moreno 2011; Wever, Picchioni and Broekhuis 2011).This may be true in the case of lesser concentrated oil-field brines, such as calcium chloride etc. Also, bromide brines are incompatible with xanthan as they rapidly degrade the polymer molecules by acid hydrolysis. However, the sheer mass of formate salt capable of dissolving in water, to yield extremely low water activities, makes the formate brines so unique in characteristics especially in respect to their compatibility with xanthan gum (Howard 2009).

From section **3.2**, results have demonstrated that the viscosity of xanthan gum solutions (along with some other biopolymers) does not decrease in the presence of highly concentrated formate brine as expected, but in fact viscosity generally increases from that of water. With that said; to better understand xanthan hydration in saturated formate brines, viscosities of each stock solution were measured before any heat exposure and outlined in **Table 3.4**. Most authors agree that the optimum pH for xanthan hydration is around 7-8 (Glass et al. 1983, Garcı́a-Ochoa et al. 2000, Seright and Henrici 1990) so samples were removed of any residual buffer and the pH corrected to around neutral for consistency. Newtonian brine viscosities were subtracted from the viscosified brines to illustrate purely xanthan contribution.

Table 3.4 Viscosities of Xanthan Solutions (8.57g/L) in Various Carboxylic Brines

Brine	**Density (g/cm^3)**	**Salt Concentration (mol/L)**	**Water Activity (A_w)***	**Initial Brine Viscosity (cP @ 50°C)**	**Viscosity – initial brine viscosity (cP @ 50°C)****	**Gel Strength (10s/ 10m)**
De-ionised water	0.999	0	1.0	1	45 (+/-2)	21/25
Sodium formate	1.32	8.8	0.625	6	69 (+/-2)	23/32
Caesium formate	2.22	10.1	0.334	5	97 (+/-3)	27/71
Potassium formate	1.42	10.1	0.458	3	67 (+/-1)	23/31
Potassium formate	1.57	14	0.238	9	90 (+/-2)	20/30
Monoethylene Glycol	1.11	0	0.034	9	109 (+/-4)	9/28

***Water Activities were measured @25˚C on Labmaster water activity meter.**
****Duplicates were measured and averages were taken.**

According to results in **Table 3.4**, the viscosity of xanthan solutions generally increase with increased formate salt concentrations, the exception being caesium formate at 10.1mol/L which is far more viscous than in potassium at a similar concentration. This phenomenon is better explained in section **3.3.5.**

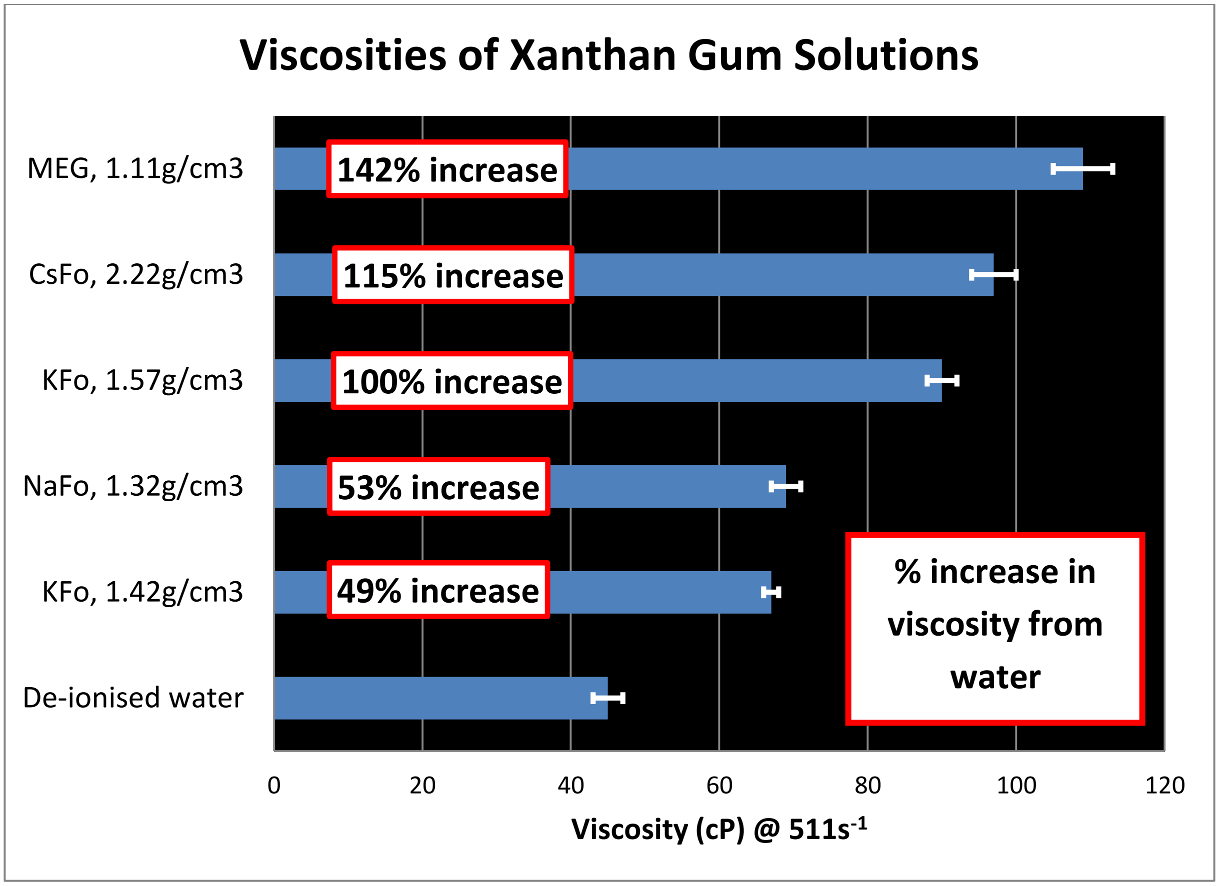


Figure 3.20 *Fann35 viscosities at 511s^{-1} of 8.57g/L xanthan gum in solution with various solutes*

These results, in contradiction to Moreno, 2011 and Fink, 2011; demonstrate that xanthan gum exhibits significantly greater viscosities in highly concentrated formate brines, than in de-ionized water where viscosity generally develops further with increasing salt concentration (see **Figure 3.20**). In fact, the viscosities of xanthan solutions actually increase with decreasing water activity which is an interesting anomaly. In agreement with these novel findings, was a study from the field of biotechnology, Garcia-Ochoa *et al*. 2000 who discovered that adding a large amount of salt to xanthan solutions of a sufficient anionic biopolymer concentration, actually raised fluid viscosity because of increased interaction between the polymer molecules, due to lack of "free space" in solution (Garćıa-Ochoa et al. 2000). Also in agreement, Wyatt *et al*. 2011 proposed that if the concentration of monovalent salt ions in solution exceeds the polymers counter ions available for intermolecular repulsion (which it would do in each of these formate solutions), then the electrostatic interactions will be screened allowing polymer chains to come into much closer contact and form a strong intramolecular network driven by hydrogen bonds. The effect is therefore notably more significant with regards to viscosity compared to polymer intermolecular associations that occur in pure water (Wyatt, Gunther and Liberatore 2011). However, Zhong *et al*. 2013 hypothesized that salt addition increases viscosity in aqueous xanthan solutions of sufficient biopolymer concentration, as it enhances intermolecular interaction by inducing local charge inversion and subsequent chain expansion. Further, there has been evidence that ion bridging may occur where either an intra or intermolecular ionic cross-link is formed to introduce a stiffer network (Zhong et al. 2013). All of the above are logical reasons to explain why xanthan viscosity develops further with decreasing water activities and increasing salt concentration in formate solutions. But essentially, one way or the other; lack of "free space" means individual polymer chains cannot move past one another as easily in solution which allows more intricate inter or/and intramolecular bonds to form.

However, for contemplating gel strengths developed in xanthan viscosified formate solutions in comparison to water, the present research complies with oil-field literature, suggesting that higher gel strengths are immediately produced in more salt concentrated solutions because of the much greater particle mass (Moreno 2011). Also in agreement, Downs, 1991 observed a reduction in pseudoplasticity (shear thinning effect) with increasing sodium formate salt concentration in comparison to water, which was also true for all concentrated formate brines evaluated in the current study (Downs 1991).

Furthermore, to examine the theory that biopolymers must have free water in order to hydrate and viscosify the fluid (Moreno 2011), xanthan was sheared into non-aqueous, low molecular weight monoethylene glycol (MEG) to see if the biopolymer would dissociate in the absence of water. Surprisingly, xanthan hydrated more strongly in the glycol than it did in any of the formate brines, and produced more than twice the viscosity yield of pure water at the same biopolymer concentration. A similar anionic polysaccharide; welan gum (discussed previously in section **3.2**) is renowned to be soluble in polar organic solvents such as ethylene glycol which produces a higher viscosity than in aqueous solution. The central conclusion for this effect is that ionic interactions are far more significant in these solvents as they occupy a lower dielectric constant which can enhance the forces between charged polar groups on specific polymer molecules in comparison to water (Member and Morris 1995). Thus, according to **Figure 3.20**, xanthan seems to manifest a similar reaction in MEG as proposed for welan gum, so in the absence of salt and water, polymer electrostatic interactions can become stronger in certain non-aqueous fluids.

3.3.3 Xanthan Stability in Caesium and Potassium Carboxylic Brines

***Refer to section 2.1.8 & 2.1.10 to measure 16-hr stability and T_m values**

To evaluate the overall stability of xanthan gum in caesium and potassium formate brines under high temperature conditions, 16-hr dynamic ageing measurements and transition temperatures (T_m) were determined.

Table 3.5 16-Hr Temperature Stability of Xanthan gum (8.57g/L) in Formate brines

Brine	pH (AHR 150°C)	Initial Brine Viscosity @ 50°C (cP)	Starting viscosity (cP)	50% viscosity loss (cP)	16-hr Stability "present study" (°C)*[2]	16-hr Stability Formate Manual (°C)*[3]
De-ionized Water (0.999g/cm^3)	6.27	1	45 (+/-2)*	23	97 (+/-3)	100
Sodium formate (1.32g/cm^3)	6.75	6	58	32	166 (+/-6)	166
Caesium formate (2.20g/cm^3)	9.56	5	41	23	166 (+/-2)	NA
Potassium formate (1.57g/cm^3)	6.6	9	85	47	178 (+/-1)	180
Caesium acetate (2.20g/cm^3)	9.51	22	95	58.5	163 (+/-0)	NA
Cs/K formate blend (2.0g/cm^3)	9.06	6	53	29.5	172 (+/-2)	NA
Cs/K formate blend (1.80g/cm^3)	7.98	7	85	46	175.25 (+/-2.5)	NA
Caesium Acetate/ Formate (50:50 blend 2.20g/cm^3)	9.62	10	78	44	163 (+/-3)	NA

***Water starting viscosity is recorded before hot-rolling (BHR), and not AHR@150°C as it degrades almost completely at this temperature. Duplicates were measured for a more representative result (all within, +/- 2cP).**

***[2] One duplicate for each test and average value displayed in Figure 3.21.**

***[3] Data from the Formate Manual was taken from section B5 (Howard, 2009)**

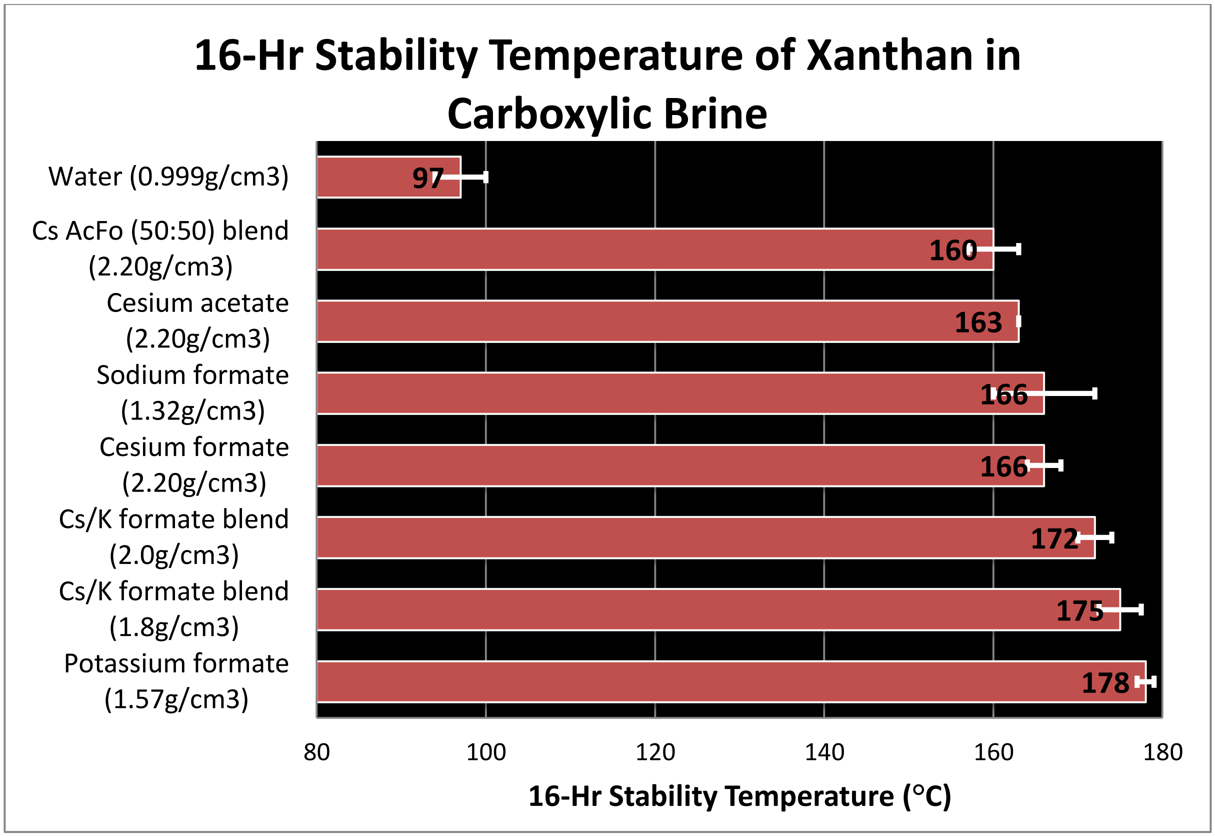


Figure 3.21 *16-Hr stability limit of 8.57g/L xanthan gum in the various concentrated brines*

Using graphs similar to **Figure 2.5** to estimate 16-hr stability temperature of xanthan gum in each of the brines, it can be concluded from **Figure 3.21** that xanthan has the highest 16-hour temperature stability limit in potassium formate; however it is clear that all of the formate salts significantly protect the biopolymer from premature oxidative and hydrolytic degradation at high temperatures in comparison to water. The greater stability in highly concentrated solution is thought to be associated with the nature of the helix-coil conformational transition (Downs 1991, Howard 2009). The excess salt makes the polymer structure in solution more compact, with increased interaction between the charged trisaccharde side chains, therefore favouring the rigid double-stranded helical arrangement of xanthan gum (Garćia-Ochoa et al. 2000). In spite of this, it has since been hypothesized in section **3.2**; that the "high salt limit" present in these concentrated formate brines "screens" the charges on polyelectrolytes to render them non-ionic, so interactions between the charged groups will become negligible and stronger intramolecular hydrogen bonding will prevail, according to Wyatt *et al*. 2011 (Wyatt, Gunther and Liberatore 2011). However, it is impossible to know for certain the exact mechanism for the improved stabilization of xanthan by formate salt without the use of more advanced characterization techniques, as solution rheology only becomes increasingly more complex at higher temperatures.

In general, xanthan stability increases with increasing monovalent salt concentration which is in close agreement with results in **Figure 3.21** as potassium formate at saturated density has a higher molar concentration than any of the other brines tested in this study (14mol/L). The 16-hr stability temperature also declines with decreasing salt concentration, for all brines (with the exception of 50:50 CsAc CsFo blend) which seem to bear a negative effect when administered in combination with one another. The clear advantage formates have over alternative monovalent brines, such as sodium chloride with regards to stabilizing polymers is that they can solubilize to far greater concentrations in water (Howard 1995). Thus, aside from their additional antioxidant, water-structuring properties; the main stabilizing mechanism of the formates is that they are very concentrated in solution, which allows very little “free-space” so the polymer chains are forced closer together to form a more rigid ordered network.

For applications in the field, caesium and potassium formate are commonly blended for intermediate densities to keep the salt concentration high and reduce overall cost of the brine – as caesium formate is a lot more expensive than potassium. Normally, the only reason density would be decreased using water instead of a lower density brine is to reduce TCT (true crystallization temperature). **Table 3.5** illustrates that adding a relatively small proportion of potassium formate to caesium, increases the temperature stability of xanthan by a further 10ºC. At the lower density blends, with a higher ratio of stock potassium formate and a greater overall salt concentration, xanthan stability is increased even further (see section **3.3.4**).

In agreement with the current study, previous literature shows that xanthan in potassium formate acquires the highest 16-hr stability limit and transition temperature profile in comparison to similar high density formate brines (Downs 1991; Howard 2009). These studies have also indicated that 16-hr stability temperature is strongly related to xanthan's transitional or melting temperature (T_m) therefore it is assumed that the other alkali-metal salts will follow a comparable stability trend when measuring T_m in the same fluids.

Table 3.6 Transition Temperatures (T_m) of Xanthan in Formate Brines (unbuffered)

Formate Brine	**Density of Brine (g/cm^3)**	**pH (brine + xanthan)**	**Transition Temperature [current study] (°C)***	**Transition Temperature [Formate Manual] (°C)*^{2}**	**16-Hr Stability [current study] (°C)**	**16-Hr Stability [Formate Manual] (°C)*^{2}**
Sodium	1.32	7.41	185	182	160	160
Potassium	1.57	6.64	199	201	177	<180 (1.59g/cm^3)
Caesium	2.2	6.69	177	157	164.5	NA

***All transition temperatures were measured on BHR fluid with one duplicate.**

***^{2}Data from the Formate Manual was taken from section B5 (Howard 2009)**

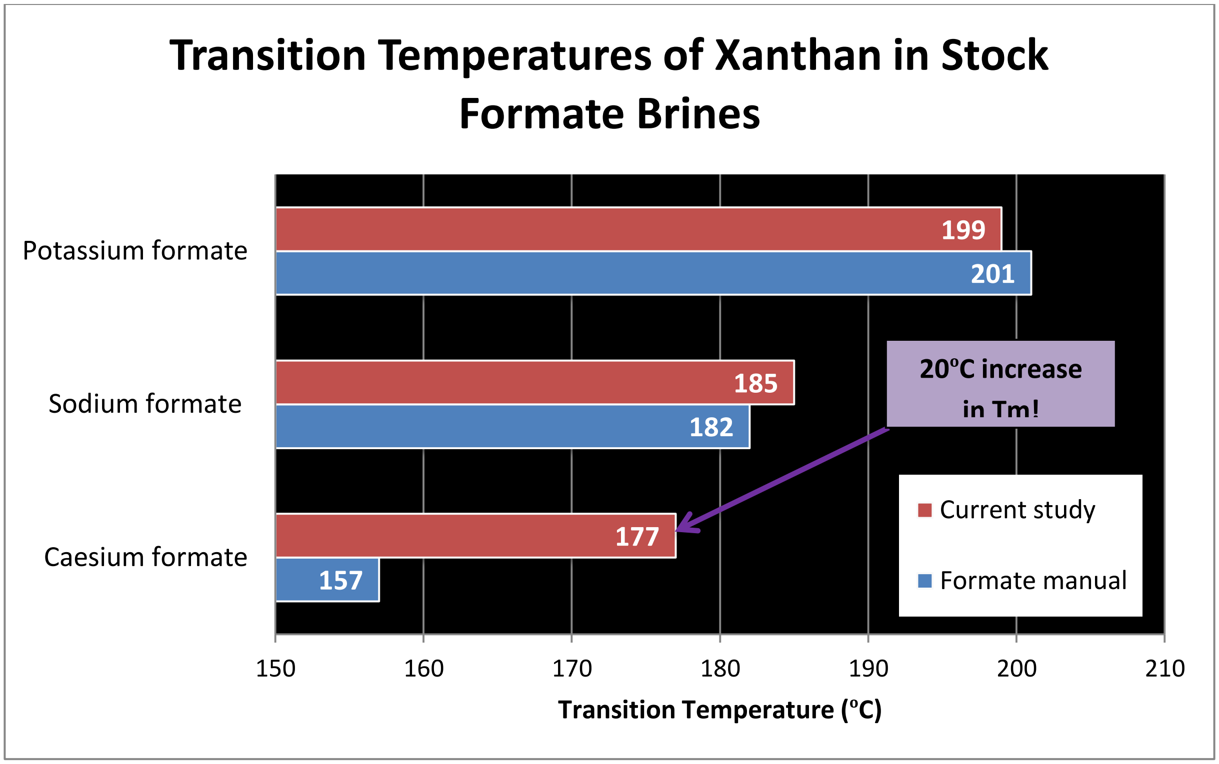


Figure 3.22 *Differences in measured T_m of xanthan gum (8.57g/L) in caesium, potassium and sodium formate from current study compared to already published data from Formate manual (Howard 2009)*

Results from **Figures 3.21 & 3.22** with regards to 16-hr stability and transition temperatures of xanthan in water, sodium and potassium formate brine are generally in agreement with Howard, 2009; and the *Cabot Specialty Fluids* Formate Manual (Howard 2009). However, the measured T_m for xanthan in 2.20g/cm^3 caesium formate is 20ºC higher than previously recorded – which is a significant finding with respect to promoting its stabilizing potential. With that said, the current caesium formate stock has a larger content of contaminants than ever before which may account for the increased T_m, as the lighter impurities can occupy more "free space" in solution, promoting the rigid double helix conformation of xanthan gum. Also, the data measured for the Formate manual was evaluated using pure grade caesium formate from Chemetall, which in turn will have a higher water activity (A_w) due to lack of contaminants allowing more "free space" for decomposition reactions to be able to occur. The MARS III modern HPHT rheometer measures viscosity with air bearings on the rotor, whereas the older style rheometer would have used mechanical bearings, which will not give as accurate readings so perhaps measuring technique is crucial for specific samples.

The current study has also established 16-hr biopolymer stabilities for brines not previously classified in literature for example, caesium acetate, formate blends etc. re-iterating the relevance of the present research.

3.3.4 Xanthan Stability in Caesium/Potassium Formate Blended Brines

***Refer to section 2.1.10 to measure T_m values**

As previously mentioned in section **3.3.3**, it is common practice in the field to blend caesium and potassium formate brines for additional benefits between densities 1.57g/cm^3 and 2.20g/cm^3. One of these benefits is superior polymer stabilization as blending the two, instead of adding water increases the overall formate molar concentration.

In order to evaluate the most favourable Cs/K formate brines for maximum stability, xanthan transition temperatures and 16-hr stabilities were measured for the standard blends and plotted in **Figure 3.23**. A caesium/potassium formate "standard blend" represents a solution prepared solely from stock brines (1.57g/cm^3 potassium and 2.20g/cm^3 caesium formate) so the ratio of caesium/potassium formate molecules can easily be determined. However, Cs/K formate "field" brine is almost never a standard blend because of the CSF recycling process which often means diluting with other non-standard brines or water, so the definition of a fluid mixed with anything other than stock density caesium or potassium formate i.e. adding or removing water, is known as a "non-standard blend."

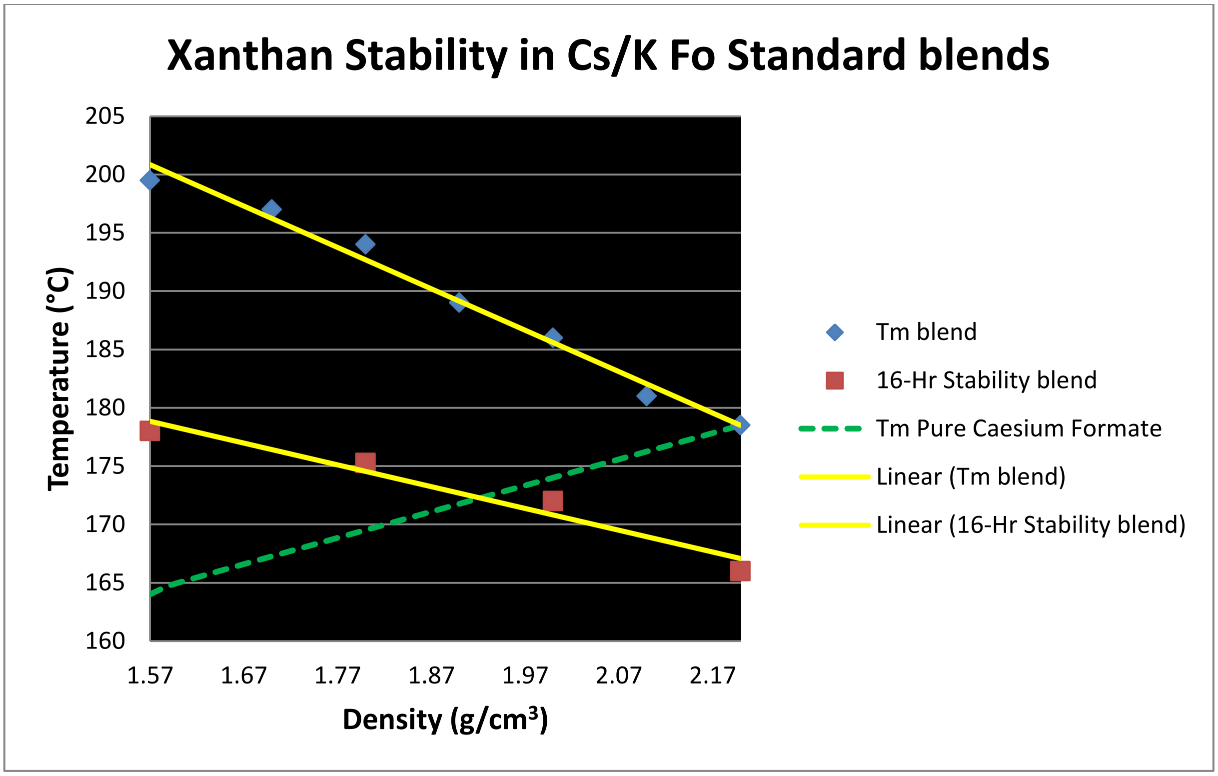


Figure 3.23 *Xanthan's (8.57g/L) transition temperature (T_m) and 16-hr stability of caesium/potassium formate standard blends*

Since potassium formate is the better stabilizer, xanthan T_m and 16-hr stability decreases with increasing density and caesium concentration – but is still a vast improvement to the stability (or T_m) measured in pure caesium formate brine (see. dotted green line in **Figure 3.23**). Thus, results from this section reconfirm the obvious benefits of blending caesium/potassium formate brines for intermediate densities (1.57g/cm^3 -2.20g/cm^3).

A further observation gathered from the standard blend results, is that xanthan stability generally improves with decreasing water activity. To put this theory to the test; a variety of non-standard Cs/K formate blends were prepared by boiling standard brines to higher densities and re-testing their xanthan transition temperatures.

Figure 3.24 Difference in Xanthan T_m between standard and non-standard Cs/K formate blends

Density of std. blend (g/cm^3)	**Density of non-std. blend (g/cm^3)**		**Water Activity (A$_w$ @ 25°C)***		**Transition Temperature (°C)**	
	Initial Density	Density After Boiling	Std. blend	Non-std.blend after boiling	Std. blend	Non-std.blend after boiling
1.70	1.60	1.65	0.268	0.182	197	201
1.80	1.70	1.80	0.275	0.152	194	197
1.90	1.80	1.90	0.282	0.188	189	192
2.0	1.90	2.0	0.29	0.187	186	188
2.1	2.0	2.1	0.295	0.189	181	184

***Water Activities were measured @25˚C on Labmaster water activity meter.**

****All fluids were un-buffered and had pH 6-7 for consistency.**

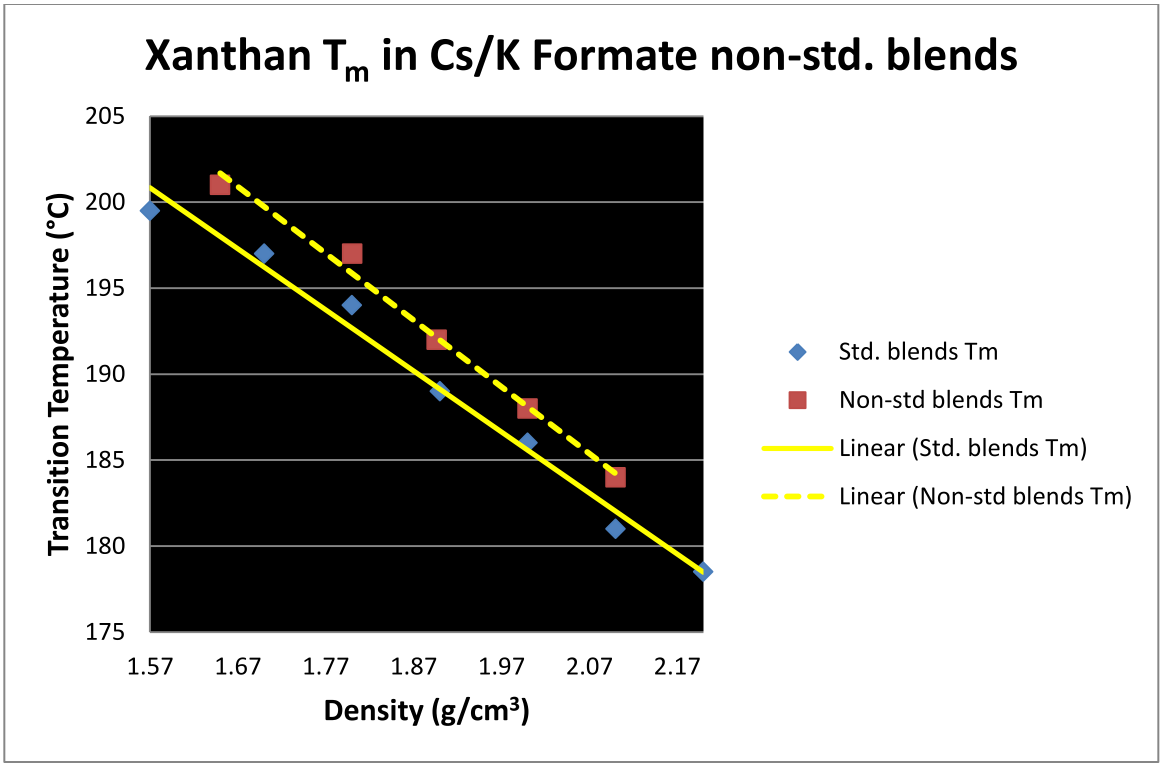


Figure 3.25 *Xanthan (8.57g/L) transition temperature (T_m) in caesium/potassium formate standard and non-standard brines*

Results from **Figure 3.25** confirm that evaporating water to increase the density does in fact, increase T_m by around 3ºC without increasing the ratio of stock potassium (1.57g/cm^3) to caesium formate (2.20g/cm^3) solution. Therefore, decreasing water activity and maximizing formate molar concentration does preferentially increase xanthan stability as expected, however it is still not as effective as directly increasing the proportion of saturated potassium formate added to the blend. Whether this is purely due to the higher molar concentration in stock potassium (14mol/L) compared to caesium formate (9.9mol/L) or a genuine effect of the cation - will be discussed in section **3.3.5**.

3.3.5 Comparing Xanthan Properties in Caesium and Potassium Formate on a Molar Basis

***Refer to section 2.1.10 to measure T_m values**

Considering previous results from section **3.3.3**; comparing 16-hr xanthan stability tests and transition temperatures of the various brines, it can be concluded that potassium formate (1.57g/cm^3) prolongs xanthan degradation to higher temperatures than any other formate fluid. Nevertheless, potassium formate has a far higher molar concentration at saturation density compared to any of the other brines, which is thought to be the reason for its superior ability to stabilize biopolymers.

Table 3.7 Molar concentration of carboxylic brines at near saturation (Howard 2011b)

Brine Type	**Density (g/cm^3)**	**Molar Concentration (Mol/L)**	**% Salt in Soln. (Mol%)**
Sodium formate	1.32	8.8	18
Potassium formate	1.57	14	39.1
Caesium formate	2.2	9.9	28.2

Therefore, to understand xanthan stability in caesium and potassium formate without the concentration variable, solutions of caesium and potassium formate were prepared using the same molar concentration (10.1mol/L) to evaluate any direct effects of the cation in increasing the temperature stability of xanthan gum.

- 1.42g/cm^3 potassium formate, pH 6.6, no buffer
- 2.22g/cm^3 caesium formate, pH 6.9, buffer removed

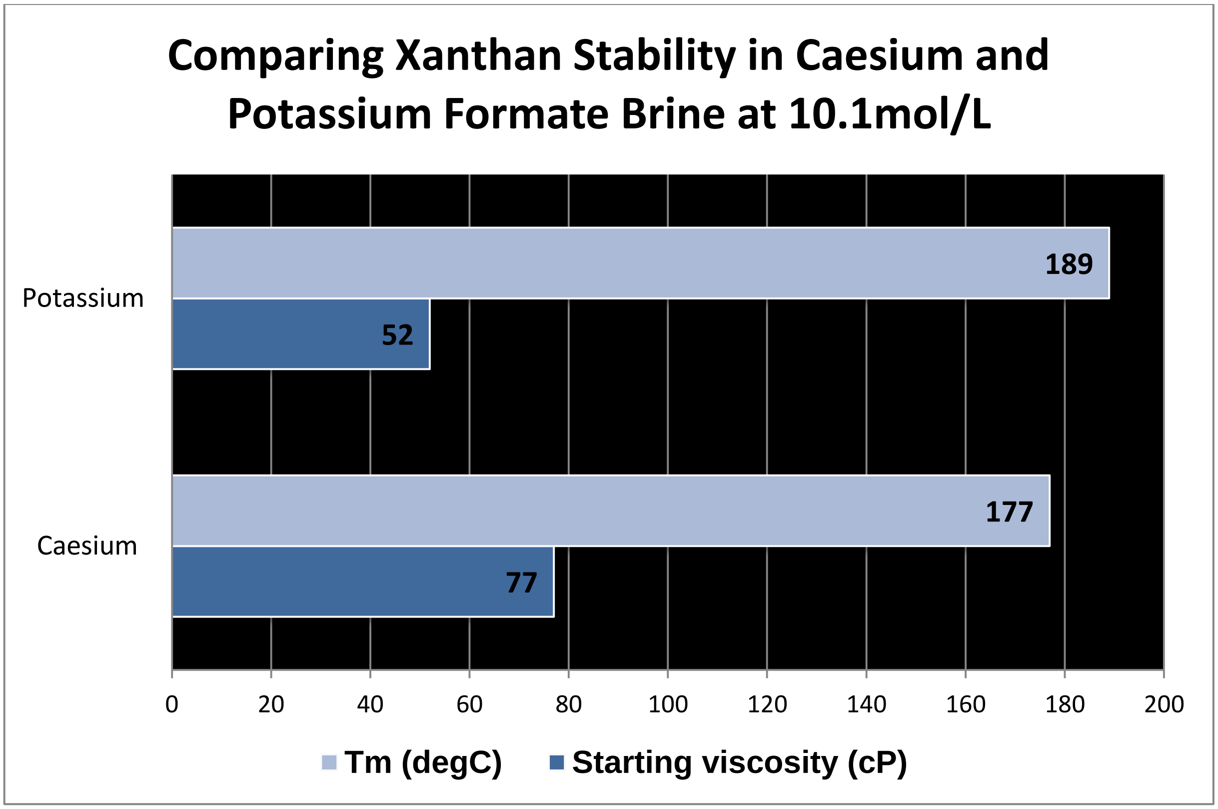


Figure 3.26 *Transition temperature (T_m) and viscosities of caesium and potassium formate brine with 8.57g/L Xanthan at the same molar concentration*

At comparable molar concentrations, results from **Figure 3.26** confirm that potassium formate is still superior to caesium at prolonging xanthan degradation, according to the measured transition temperature – so altering the cation has a genuine influence on xanthan stability. This effect of the cations will be discussed further in section **3.3.6**. However, when comparing starting viscosities (AHR@150ºC), the same concentration of biopolymer generates more than 30% extra viscosity in caesium formate than in potassium formate. This phenomenon can possibly be explained by conclusions gathered from section **3.3.2**, where caesium formate is much closer to saturation density at 2.20g/cm^3 than potassium at 1.42g/cm^3, so the molecules in solution are more tightly packed together which forces increased interaction between the polymer chains. Moreover, Lei and Clark, 2004 suggested that salts with large bulky cations (such as caesium) will minimize the screening effect in polymers, compared to potassium and sodium which are particularly effective at screening charges in solution (Lei and Clark 2004). So the larger size of the caesium cation compared to potassium can promote further electrostatic interaction between the xanthan trisaccharide side chains to stretch the polymer molecules due to decreased screening efficacy. In addition, caesium formate has a far lower water activity of 0.334 A_w at 10.1mol/L than potassium (0.458A_w) so this corroborates the trend suggested in section **3.3.2** that viscosity of formate xanthan solutions increase with decreasing water activities. Previous literature also has highlighted that with regards to salts, varying cation size and valence in polymeric solutions can massively affect rheology (Wyatt, Gunther and Liberatore 2011).

Conclusions of this study combined with extensive literature research, has made it clear that xanthan hydrated in solution with concentrated formate brine has a unique behaviour which is largely dissimilar to that of water-soluble polymers dissolved in traditional brines still used in the oil-field industry today. This is due to their ability to increase the viscosity yield of xanthan, as opposed to decreasing it by shielding ionic interaction.

3.3.6 The Cation Effect on Xanthan Stability

***Refer to section 2.1.10 to measure T_m values**

Since the formate anion ($HCOO^-$) is a powerful "salting-out" water structure maker, it is thought to be the reason for the enhanced polymer stability observed in alkali metal formates, affiliated with their unique ability to solubilize to high concentrations in water (Howard 1995). However, knowledge learned from section **3.3.5** has confirmed that the higher molecular concentration of formate in solution is not the sole justification for superior polymer stability and thus the conjugate metal cation also contributes to the effect in some way.

Subsequent to the original Hofmeister series of anions arranged in order of their increasing ability to "salt out" proteins and macromolecules, it was soon recognized that the associated cation can also affect the hydrogen bonding network of water in a similar manner (Marcus 2012). However, the effect is subsidiary to the dominant role of the anion in promoting the Hofmeister response largely due to the repulsive interactions of positive charges at the active sites on the polymer chain. Nevertheless, the Hofmeister series for cations has been established for a given anion (Tóth et al. 2008):

$$K^{+} > Na^{+} > Cs^{+} > Li^{+} > Mg^{2+} > Ca^{2+} > Ba^{2+}$$

To investigate whether the Hofmeister effect for cations is true for alkali metal formates; monovalent lithium, sodium, potassium and caesium brines were prepared at similar formate molar concentrations (5mol/L) and their xanthan T_m was measured using the Haake MARS III HPHT rheometer pressure cell.

Table 3.8 Xanthan T_m of Formate brines at 5mol/L concentrations

Formate Brine	Density (g/cm^3)	Transition Temperature (°C)	Water Activity (Aw @ 25°)*
Lithium	1.15	160.5 (+/-0.5)	0.752
Sodium	1.20	164.5 (+/-0.5)	0.784
Potassium	1.23	166.25 (+/-0.25)	0.756
Caesium	1.61	164.5 (+/-0.5)	0.755

***Water Activities were measured @25˚C on Labmaster water activity meter.**

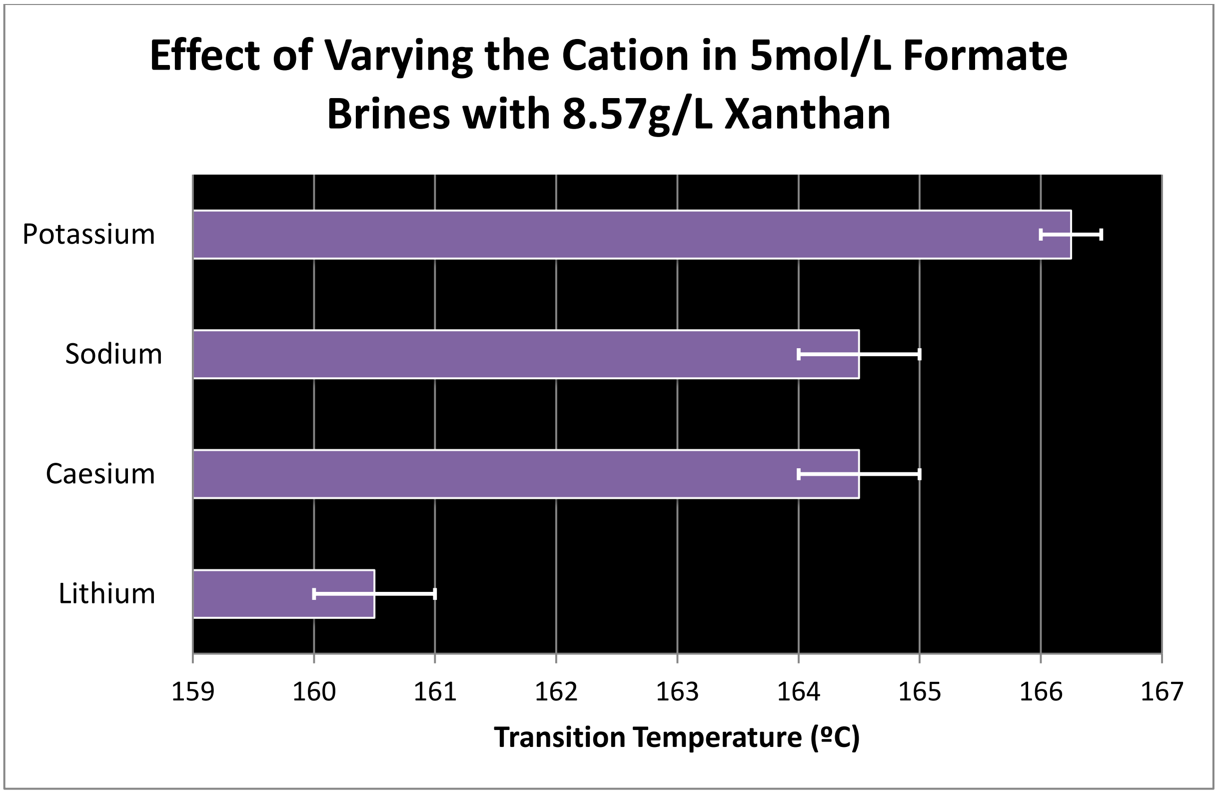


Figure 3.27 *Xanthan T_m in 5mol/L lithium, sodium, caesium and potassium formate solutions*

According to **Figure 3.27**, at similar formate molar concentrations; the sequence of cation "salting out" effects generally follows the Hofmeister series though only slight differences in T_m separate the cation's stabilizing abilities, which is in close agreement with previous studies (Marcus 2012; Tóth et al. 2008). However, in the more concentrated solutions (e.g. 10.1mol/L, see section **3.3.5**), the cation's effect is clearly more conclusive as potassium formate T_m is 12ºC higher than caesium formate at the same molar concentration. A credible explanation for this is; the formates unique ability to solubilize to high concentrations in water, allows the Hofmeister effect or "salting-out" of cations to become more pronounced as the solution becomes more saturated.

Results from **Figure 3.27** illustrate that the stabilizing potential of xanthan gum in caesium and sodium formate at 5mol/L are the same, although sodium formate according to the Hofmeister effect of cations should be slightly higher. The sodium formate salt utilized to create the 5 mol/L brine was analytical grade and therefore should contain very little residual impurities, whereas current stock caesium formate has a slightly higher volume of contaminants than usual i.e. sodium, lithium etc. – see section **3.3.3**. Since the density for the 5 molar caesium formate solution was referenced from the Formate manual (Howard 2009), it assumed that all dissolved material is pure caesium formate, and therefore to apply those values to the current stock – will result in a slightly higher molar concentration as it does not account for the excess contaminants. These excess salt "contaminants" can contribute to salinity and may be accountable for the slight increase in xanthan T_m. Further, **Table 3.9** illustrates that sodium formate has a slightly higher water activity than the others (perhaps due to lack of contaminants), which could also potentially contribute to a reduction in T_m according to results from section **3.3.4**.

3.3.7 Buffer and pH Effects on Xanthan Stability in Caesium and Potassium Formate Brine

***Refer to section 2.1.8 & 2.1.10 to measure 16-hr stability and T_m values**

With regards to water-soluble polymers, it has been well documented in literature that altering pH can affect hydration properties in oil-field brines (Norton, Spyropoulos and Cox 2010; Glass et al. 1983). However, there are limited research studies on the effect of buffer and/or pH on the stability of biopolymers at high temperatures – especially in the alkali metal formates. Therefore, xanthan stability tests were implemented to conclude whether the carbonate/bicarbonate buffer system does actually affect the biopolymer's viscous characteristics or conformational transition temperature (T_m) and if so, to what extent in concentrated caesium and potassium formate brines.

All of the formates are naturally alkaline in nature, but on this occasion the stock potassium formate at 1.57g/cm^3 has a measured pH in between 6 and 7, whereas concentrated caesium formate (2.20g/cm^3) has a pH of around 10-10.5. Stock potassium has no added buffer whereas the caesium formate stock has the equivalent of 18g/L potassium carbonate/bicarbonate buffer (13.3g/L K_2CO_3 and 5g/L $KHCO_3$), which can inhibit polymer hydration – as observed in section **3.2.5**.

Table 3.9 16-hr Temperature Stability for Caesium and Potassium Formate with 8.57g/L xanthan, buffered and unbuffered

Brine Type	**Density (g/cm^3)**	**pH (brine + xanthan)**	**Buffer? (Y/N)**	**Starting viscosity AHR@150ºC**	**50% Viscosity Loss (cP)**	**16-hr Stability Temp (ºC)**
Caesium formate	2.20	10.2	Y (13.2/5gL carb/ bicarb)	41	23	164.5
Caesium formate	2.20	9.7	N	75	40	166.5
Caesium formate	2.22	6.9	N	77	41	165
Potassium Formate	1.57	9.2	Y (3.31/9.22gL carb/ bicarb)	84	46.5	171.25*[2]
Potassium formate	1.57	6.6	N	87	48	178*[2]
Potassium formate	1.57	9	N	87	48	179

***16-hr stability temperature was measured using a plot of 16-hr hot roll temperature (ºC) vs. viscosity (cP), chapter 3.5.**

***[2]Average (16-hr stability temperature), one duplicate.**

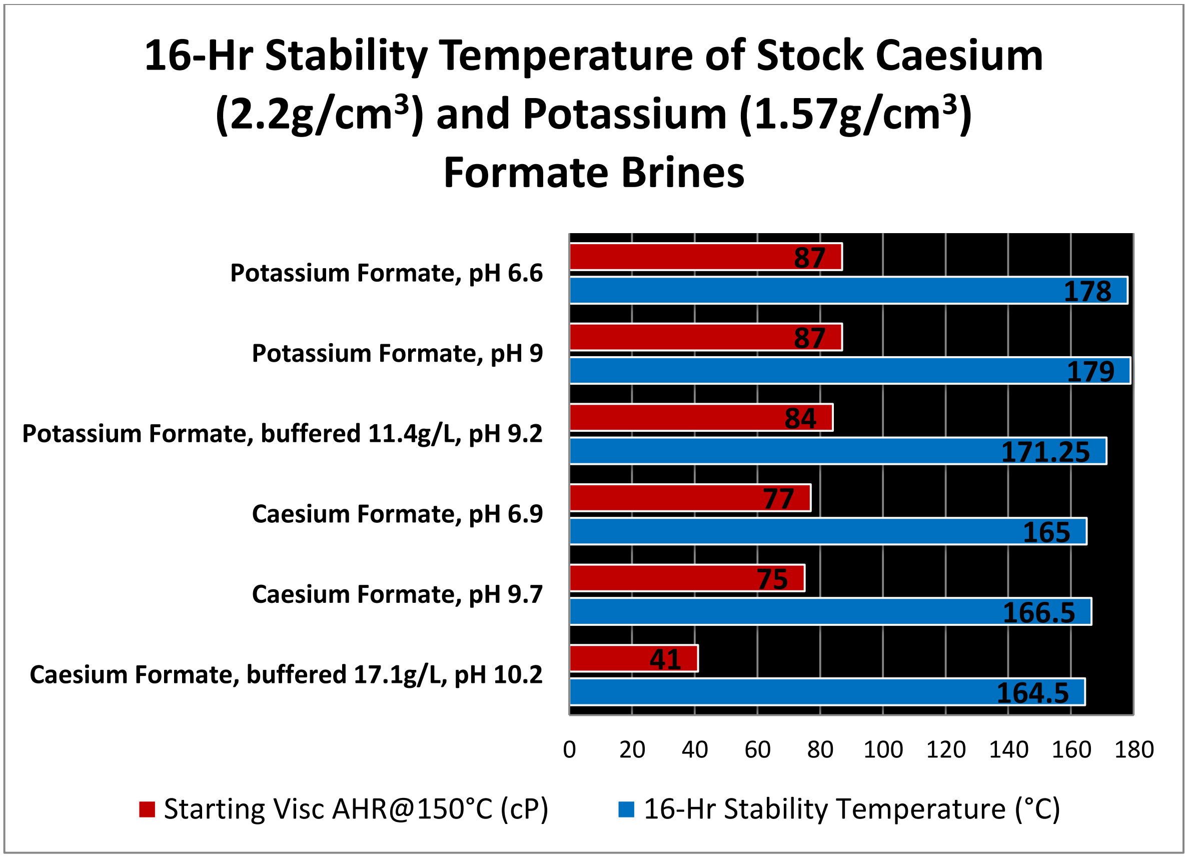


Figure 3.28 *16-Hr stability temperatures for caesium and potassium formate stock brines varying buffer levels and pH*

Figure 3.28 illustrates that the presence of buffer in concentrated potassium formate stock brine can decrease 16-hr stability temperature by around 7-8°C, however the viscosity is similar to that observed in unbuffered brine at varied pH (after dynamic ageing at 150°C). In contrast, adding buffer to caesium formate (2.20g/cm^3) doesn't seem to affect the T_m much, but drastically reduces xanthan's viscosity in solution – to just over half that in the same brine with the residual buffer content removed. Worth noting is; in the unbuffered brines where pH was increased to 9-10, pH instantly drops down to around 6-7 during hot-rolling even at the lower temperatures so it is unsurprising that there are little differences in properties between unbuffered samples of varying pH. Therefore, in order to accurately evaluate whether it is solely pH or buffer content responsible for the decrease in T_m and/or viscosity, rheology profiles were recorded using the Haake MARS III HPHT rheometer pressure cell system for shorter term tests (1-2 hours) which are less likely to induce this two-to-three fold drop in pH.

Table 3.10 Transition Temperatures (T_m) of Caesium and Potassium Formate at varying pH and buffer content*

Brine Type	**Density of base brine (g/cm^3)**	**pH (brine + xanthan)**	**Buffer? (Y/N)**	**Transition Temperature (°C)**
Caesium formate	2.21	10.71	Y (41.5/6.37gL carb/bicarb)	174.5 (+/-0.5)
Caesium formate	2.20	10.1	Y (13.2/5gL carb/bicarb)	175.5 (+/-0.5)
Caesium formate	2.20	6.69	N	178.5 (+/-1.5)
Caesium formate	2.20	8.54	N	176 (+/-0)
Caesium formate	2.20	9.66	N	177 (+/-1.5)
Cs/K formate	2.0	6.66	N	187 (+/-1)
Cs/K formate	2.0	10.1	Y (8.57/4.57gL carb/bicarb)	186 (+/-0)
Potassium formate	1.58	7.45	Y (0/20.28gL carb/bicarb)	198.5 (+/-0.5)
Potassium Formate	1.58	9.97	Y (13.82/16.43gL carb/bicarb)	189 (+/-0)
Potassium formate	1.57	6.64	N	199.5 (+/-0.5)
Potassium formate	1.57	7.87	N	198 (+/-1)
Potassium formate	1.57	11.61	N	199 (+/-1)

***All transition temperatures were measured on BHR fluid with one duplicate and around 20 bar initial pressure exerted to prevent the fluid from boiling. See section for full transition temperature measurement method.**

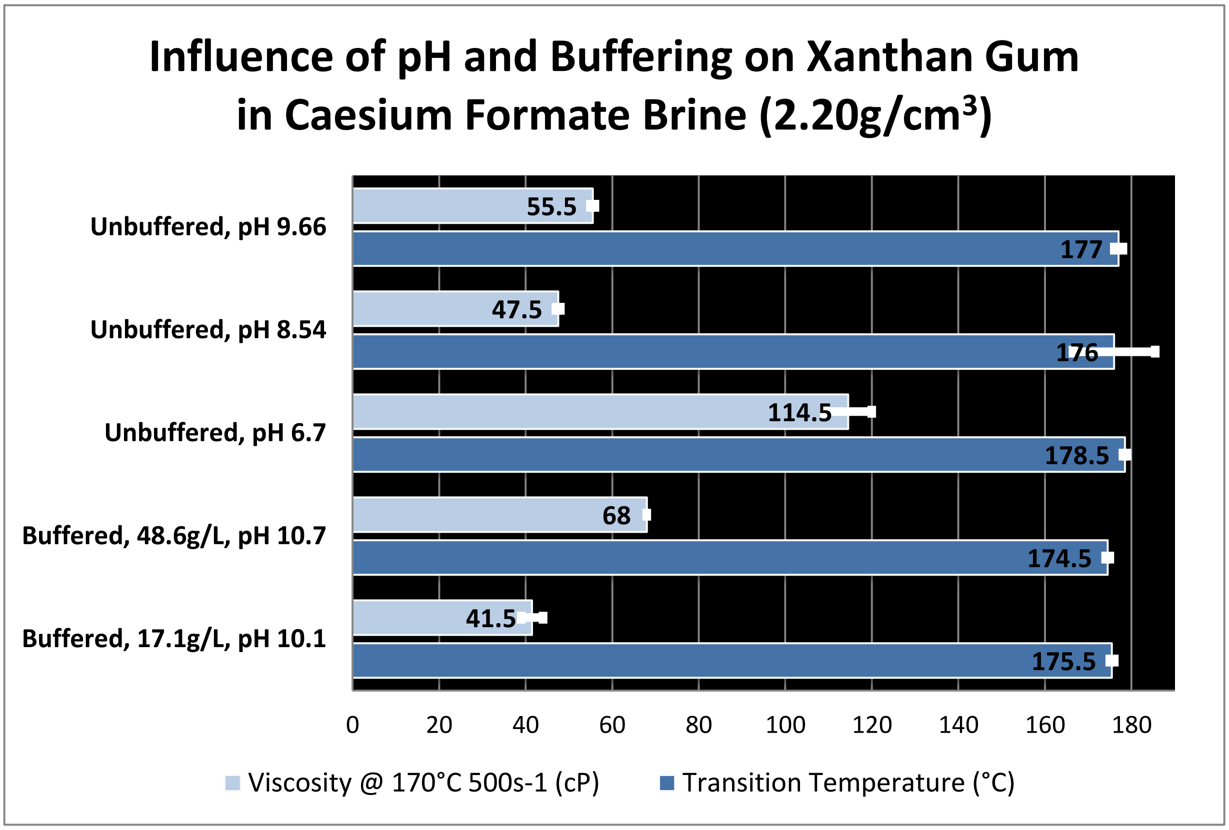


Figure 3.29 *Viscosity and transition temperatures of caesium formate brine (2.20g/cm^3), viscosity was measured at 170°C before T_m*

With regards to unbuffered caesium formate, **Figure 3.29** illustrates that lowering pH to around 7 has little effect on T_m but does however massively influence solution viscosity considering the decrease in viscosity values as the pH becomes more alkaline. This is consistent with the literature as most authors agree that the optimum pH for xanthan hydration is around neutral (Seright and Henrici 1990, Glass et al. 1983). Another interesting discovery when measuring HPHT rheology of xanthan in standard caesium formate stock brine is the presence of residual buffer (13.3g/L carbonate/5g/L bicarbonate) inhibits the biopolymer's viscosity by around 25% compared to unbuffered brine of a similar pH – and is 65% less viscous than the same solution with reduced pH. Adversely, heavily buffering the fluid actually increases xanthan solution viscosity with actual T_m only slightly reduced with carbonate/bicarbonate addition in caesium formate brine.

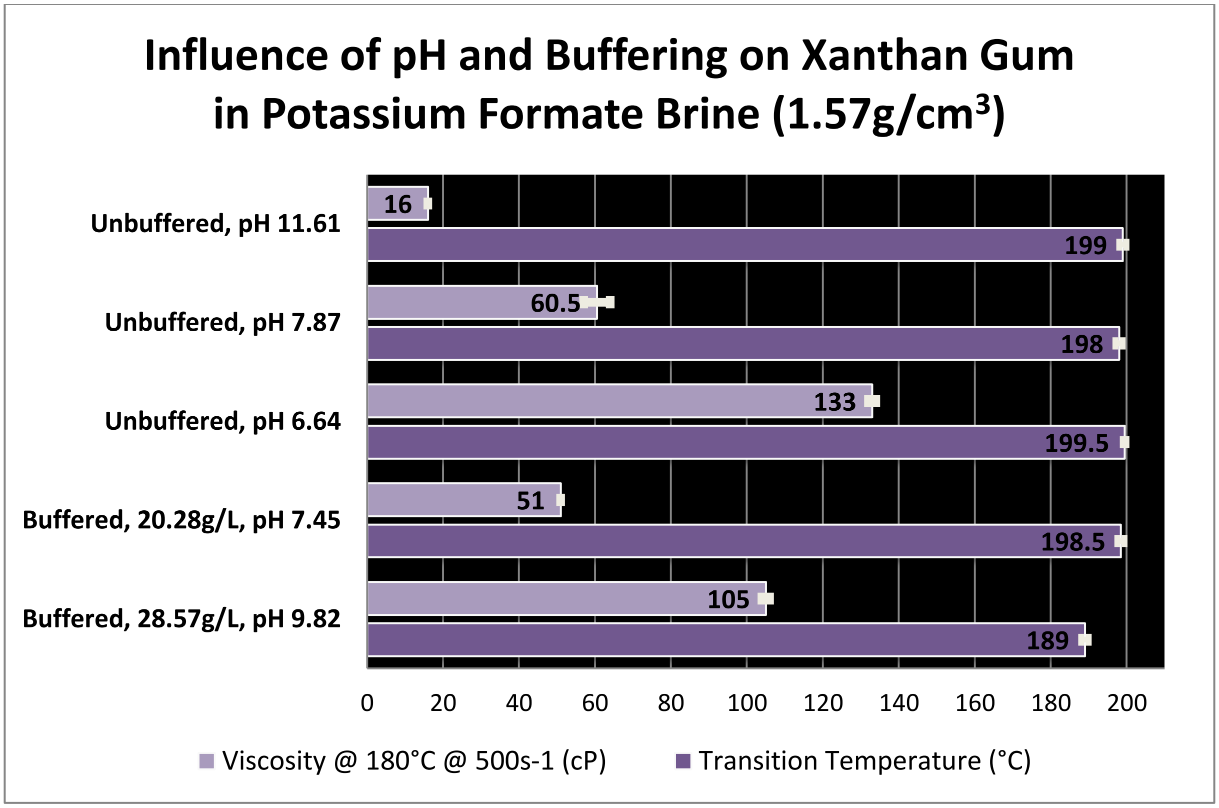


Figure 3.30 *Viscosity and transition temperatures of potassium formate brine (1.57g/cm^3), viscosity was measured at 180°C before T_m*

Comparable to stock caesium formate, **Figure 3.30** demonstrates that increasing pH in unbuffered potassium formate brine dramatically reduces solution viscosity but does not affect T_m. Literature studies suggest that between pH ranges 6-11, degradation is unlikely to occur due to acid hydrolysis or base catalysed fragmentation reactions, but changes in xanthan hydration properties are expected due to the dissociation characteristics of the polymer's carboxyl group (Moreno 2011, Norton, Spyropoulos and Cox 2010). Also, a similar trend can be observed adding buffer to potassium formate; the viscosity generally decreases with small K_2CO_3/$KHCO_3$ additions but if an excess is added, viscosity will eventually increase even in highly alkaline solution (see **Figure 3.30**). With that said, far less carbonate/bicarbonate (only 28.57g/L) will readily dissolve in potassium formate, compared to caesium at stock densities - presumably because of its higher salt concentration (14mol/L) and lower water content. Unfortunately though, the excess buffer can be detrimental to the biopolymer's stability and reduce the T_m in potassium formate by as much as 10ºC. The addition of buffer to potassium formate also reduces xanthan's 16-hr stability temperature by around 7-8°C; even at a much lower concentrations (11.43g/L).

The highest recorded transition temperatures have been discovered in xanthan products containing minimum pyruvate and maximum acetate groups in their trisaccharide chain (Downs 1991; Renou et al. 2013). However, Ash *et al*. 1983 suggested that the acetyl groups in xanthan are completely removed at pH 12, even at room temperature – so perhaps the presence of buffer in formate solutions is lowering the T_m due to progressive removal of acetyl groups at the increased pH (Glass et al. 1983). If this is true, then the effect is conceivably more pronounced in potassium formate rather than caesium, due to the higher T_m; and therefore collapse of helical aggregates becomes more sensitive at extreme temperatures (190-200ºC). It is interesting that increasing pH without adding buffer, generally does not affect T_m – wherefore a specific concentration of carbonate/bicarbonate in solution must induce a slight conformational change which either exposes susceptible sites on the polymer backbone or inhibits the hydrogen bonding network in some way. Furthermore, as observed with the 16-hr stability tests; the pH will drop rather quickly without buffer present, even with the faster tests in the MARS III rheometer – so the decreasing pH at high temperature could potentially cancel out removal of acetyl groups from xanthan's prevalent side chains if this is in fact the impeding mechanism.

The present findings are in contradiction with studies by Glass *et al*. 1983, and Levitt *et al.* 2011 who suggested that the carbonate/bicarbonate buffer increases xanthan stability by preventing measures, such as; acid-hydrolysis of the β-glycosidic backbone (Glass et al. 1983) and the auto-oxidation of iron to redox cycle (Levitt et al. 2011). Also, in a recent CSF study by Howard & Downs, 2009 on the carbonate/bicarbonate package in formate brines, they mention that the buffered brines protect water-soluble polymers by preventing the pH decreasing to a range where acid hydrolysis can persist (Howard and Downs 2009). This is more than likely true; however there has been no evidence thus far in literature or laboratory research to illustrate the direct effect of the carbonate/bicarbonate buffer with regards to the hydration and melting temperature (T_m) of xanthan gum. Therefore, measuring such effects of the carbonate/bicarbonate buffer in high density brines, such as the formates and noting unexpected differences, consolidates the significance of this novel research.

3.3.8 Using Additives to Enhance Thermal Stability of Xanthan in Potassium formate brine

Numerous stabilizing additives can be used to push the stability limits of xanthan gum to higher temperatures in high salinity formate brines. These are anti-oxidants, oxygen scavengers, cross-linkers, polyglycols and many other thermal extender products. Since potassium formate is by far the best promoter of xanthan stability at saturated densities, it was the brine of choice for testing these products in.

Table 3.11 Stabilizing Additives Trade names and Composition

Brand Name	**Generic Name/ Composition**	**Primary Function**	**Manufacturer/Supplier**
NOxygen XT	Sodium Erythorbate	Oxygen Scavenger	Baker Hughes
Oxygon	Sodium Erythorbate	Oxygen Scavenger	BAROID
PEG 200	Polyethylene Glycol (mol. weight 200g/mol)	Shale Stability	Sigma-Aldrich
PEG 400	Polyethylene Glycol (mol. weight 400g/mol)	Shale Stability	Sigma-Aldrich
Aktaflo-E	Oxyethlated alkyl phenol liquid	Surface Active Agents	BAROID
Activator II	Magnesium Oxide and Oligosaccharide/ Lignin blend	Polymer Stabilizer	M-I SWACO
MagOx	Magnesium Oxide	Alkalinity pH control	Sigma-Aldrich
Lamox NA	Sodium Hydrogen sulphite	Oxygen Scavenger	Lamberti
KI	Potassium Iodide	Antioxidant	Sigma-Aldrich
Ecco Temp	Nitrilotriethanol	Temperature Stabilizer	Baker Hughes
Rheomate	Zirconium citrate	Thinner/ Temperature Stabilizer	Lamberti
Safescav CA	Organic sulphur free additive	Oxygen Scavenger	M-I SWACO
MEA	2-Aminoethanol	Antioxidant, pH buffer	Sigma-Aldrich
MEG	Ethylene Glycol	Hydrate Inhibition	Sigma-Aldrich

After 16 hours dynamic ageing at 190ºC, xanthan in potassium formate without any additives degrades almost completely – 10cP (see **Figure 3.31**), so the various thermal extender products administered in controlled concentrations are supplemented to prolong degradation at this temperature and higher. Most of the thermal extender products listed above are acknowledged (at least in part) to;

stabilize biopolymers because of their ability to inhibit the formation of oxygen radicals which play a major role in the degradation of polysaccharides. High density formate brines are already strong antioxidants in themselves, so additional stabilizer products are normally not required for drilling and completion in the field unless BHT's are expected to be in excess of 170ºC. However, at these temperatures and above, the salt concentration becomes less effective as thermal stabilizers as the heat reduces intra- and intermolecular reactions between the trisaccharide side branches and the glycosidic backbone – so the polymer links are more readily available for chemical attack (Wellington 1983). Additives which possess anti-oxidant or scavenging qualities include; MagOx, PEG 200/400, MEG, sodium erythorbate, potassium iodide, Lamox NA, Safescav CA, MEA and Activator II. An exception to the rule includes; Aktaflo-E, an oxalated alkyl phenol liquid, which instead adds aromatic rings to the backbone of polymer chain to increase thermal stability (Moreno 2011).

In addition, Newtonian viscosities were measured for the liquid additives to confirm whether increased base viscosity could be responsible for improved stability after dynamic ageing, however all additives (5% MEG, 2% MEA, 3, 5 &7% PEG 200/400, 5.7g/L Aktaflo-E, 3% Ecco Temp, 0.5, 2% Lamox NA) altered Newtonian viscosity by no more than 1cP, so it can be concluded that base viscosity difference is negligible.

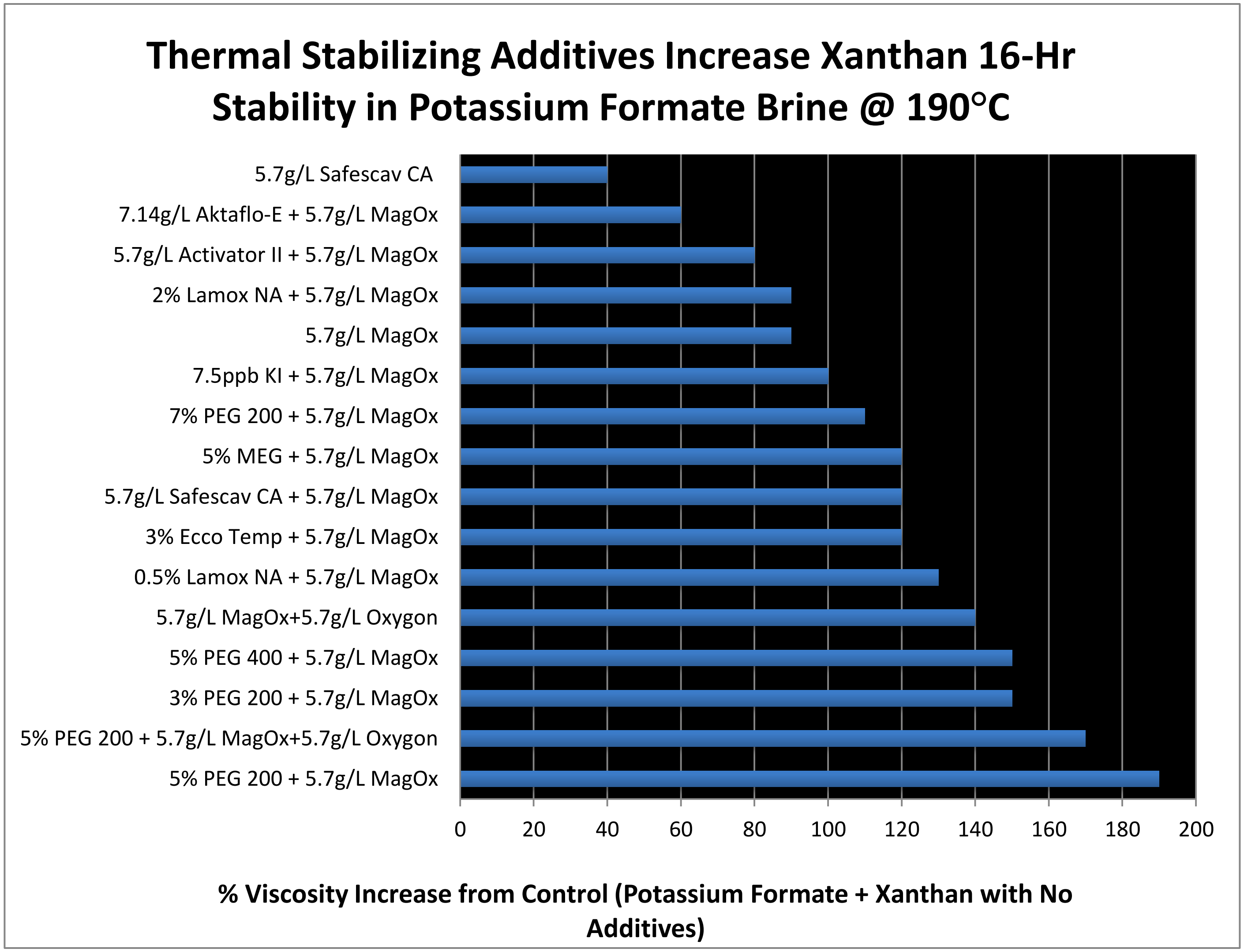


Figure 3.31 *Percentage viscosity increase from control after hot-rolling for 16 hours @ 190ºC with stabilizing additives*

Figure 3.31 illustrates the additives (or combination thereof) successful in increasing the temperature limit of xanthan gum in potassium formate brine. However, upon closer inspection of **Figure 3.31**; most additives perform at their best when combined with magnesium oxide (5.7g/L), for example; none of the thermal stabilizers in **Table 3.11** (with the exception of Safescav CA) actually improve xanthan stability exclusively after dynamic ageing for 16 hours at 190ºC and above. In fact, Aktaflo-E, Rheomate and Activator II actually decrease stability as MagOx protects the biopolymer to higher temperatures on its own. Additives which can disrupt the hydrogen bonding among pyranose units will therefore prefer the unstable coiled conformation of xanthan in solution, thus decreasing T_m and leaving the polymer backbone more susceptible for decomposition.

In absence of stabilizing additives, another factor which could promote degradation by redox cycling is residual salt contamination in the polymer (Glass et al. 1983; Levitt et al. 2011). Samples of Xanvis® were measured by SEMEDAX elemental analysis at the Robert Gordon University which illustrated a low level of counter ions and contaminants recordable in the powdered form – namely sodium, potassium, sulphur, phosphorus and magnesium (full data available in Appendix). Seright & Henrici, 1990 explicates that because of the charged trisaccharide side chain associated with xanthan, there will be a small amount of alkali metal ions (around 100ppm) present in the polymer solution, which is in close agreement to X-ray analysis gathered from RGU (Seright and Henrici 1990).

Magnesium oxide is most commonly used as a source of alkalinity or pH buffer in fluids but is often added to extend the temperature limit of polymers as it deters acid hydrolysis. Magnesium compounds such as MagOx, can also bind transition metals, inhibiting their catalytic activity for redox cycle in oxygen saturated solutions. MagOx also inhibits hydro peroxide formation to prevent oxidative degradation of the biopolymer, however Glass *et al*., 1983, observed that it was completely ineffective in solutions where a scavenger (such as sodium dithionite) had been previously added to remove the oxygen (Glass et al. 1983). In another instance, MagOx is a cross-linking activator so could potentially be initiating linkages between individual xanthan macromolecules and/or other additives to enhance further stability. Magnesium oxide is an interesting product in that it does not induce cross-linking straight away, but tends to activate over the course of a few hours (or when exposed to high temperatures). Thus, its application is especially suited for LCM or fracturing pills where viscosity is ideally maximized down hole (Horton and Prasek 2009).

Results from the present study, confirm that MagOx is a powerful additive in terms of decreasing xanthan degradation in potassium formate brine at high temperatures. **Figure 3.32** is evidence of the potential synergies of each product with MagOx.

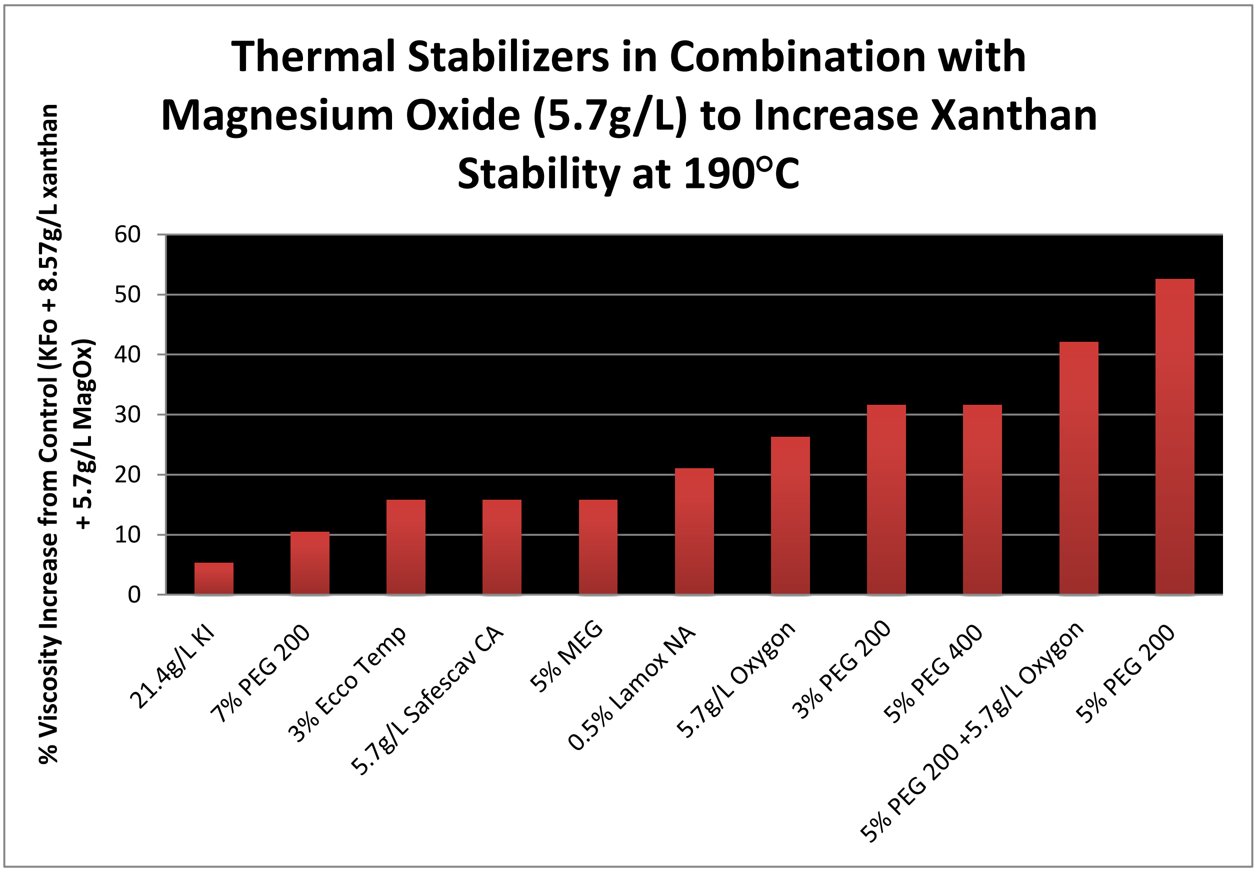


Figure 3.32 *Thermal stabilizers increase xanthan stability in combination with (5.7g/L) magnesium oxide*

All of the thermal extender products **(Table 3.11)** increased xanthan stability in potassium formate at least to some degree when administered with magnesium oxide, however the preferred additive or combination applied were; 5% (v/v) PEG 200 with 5.7g/L MagOx – which increased viscosity by over 50% from the control (control = 19cP after hot-rolling at 190ºC). In the past, polyglycols have been added to drilling fluids to provide enhanced shale stabilization or to inhibit the formation of marine gas hydrates when drilling. However, van Oort *et al*, in 1997 recognized that certain polyglycols can improve the high pressure/high temperature (HPHT) stability of xanthan and other well-known polymers in water-based fluids. Polymer and polyglycols associate by intermolecular hydrogen bonding and hydrophobic interactions; the association/complexation reactions help stabilize the polymer at high temperature. Three polyglycol types; polyethylene glycol (PEG), polyalkene glycol and fatty amine ethoxylate used in an optimum concentration of 5% (v/v) were found to enhance xanthan stability in potassium formate drilling fluid to around 190 to 200ºC. To compare with van Oort's previous findings, two of the polyglycols tested in the 1997 paper (PEG, molecular weight 200 & 400) was re-evaluated in potassium formate to conclude that the glycol itself is relatively ineffective in stabilizing xanthan to higher temperatures (190 &200ºC), unless combined with MagOx (5.7g/L). Although, magnesium oxide is not specifically mentioned in van Oort's paper, 16-hr stability was measured in water-based drilling fluids as opposed to dynamic ageing simply brine and xanthan, so oxygen scavengers/thermal stabilizer products present the mud formulation could be comprising a similar affect. To summarize, PEG added to potassium formate in combination with MagOx operates synergistically to largely improve xanthan stability, with 5% (v/v) essentially the optimum concentration for maximum stability benefits, which is in close agreement with laboratory findings by van Oort in 1997 (van Oort et al. 1997). In addition, years earlier; Wellington in 1983, agreed that a combination of sacrificial agent (e.g. glycol), high salt concentration in the brine and oxygen scavengers produce a synergistic result with regards to increasing the temperature stability of water-soluble polymers (Wellington 1983).

Other alcohols, (MEA and Ecco Temp) were also efficacious in increasing stability when used in combination with MagOx. They are thought to act as sacrificial agents similar to that of the glycols (MEG/PEG), by which they prevent redox depolymerisation by being preferentially oxidized instead of the biopolymer (Kulawardana et al. 2012). Sulphur containing antioxidants, interfere with the redox cycle by producing stable products to induce termination of destructive free radical species. Additives, such as Lamox NA which contain only one sulphur atom are the best known scavengers for the peroxide decomposing type (Wellington 1983). With that said, it is important that the concentration of additives are determined for maximum effectiveness, for example from **Figure 3.31**; 2% Lamox NA actually decreases stability in the presence of MagOx but 0.5% Lamox NA is highly efficient, highlighting the relevance of limiting antioxidant/scavenger concentration – as more is less efficient than the correctly proportioned amount.

3.4 The Effects of Synthetic Polymers in Formate Brines

3.4.1 Qualification of Synthetics

*Most of the initial qualification and hot-rolling testing on synthetic polymers in Cs/K formate were carried out by MSc student, Zhao Anderson during her three month laboratory project based at CSF.

The development of high temperature synthetic polymers in oilfield applications is on-going due to the increasing demand for environmentally friendly water-based drilling fluids which can compete with their oil-based competitors for use in more extreme operating environments. Results from section **3.3.8** have confirmed that biopolymers, such as xanthan gum can be stable up to 200ºC for 16 hours in concentrated formate brines with the aid of additional stabilizing chemistries; synthetic polymers can be employed to push these stability limits further for longer exposure times. For this reason, it was decided to systematically qualify numerous water-soluble synthetic polymers combined with xanthan gum to create a "two phase" high temperature polymer system in Cs/K formate. Similar to section **3.2.1**, buffered 2.0g/cm^3 Cs/K formate brine (13.1g/L carbonate/bicarbonate) was used, at pH 10 as a standard to compare polymer viscosities before and after dynamic ageing at 185^{o}C HPHT temperature.

Table 3.12 Synthetic Polymer Products

Brand Name®	Generic Name/Composition	Primary Function	Manufacturer/Supplier
4-mate Vis HT HML	AMPS co-polymer	Viscosifier	Fritz
ALL-TEMP	Acrylate ter-polymer	Deflocculant	Baker Hughes
AMPS 2404 (powder)	AMPS monomer	Viscosifier	Lubrizol
AMPS 2405 (solution)	AMPS monomer	Viscosifier	Lubrizol
Dristemp	Acrylamide	Fluid Loss	Drilling Specialties
HE 100	AMPS co-polymer	Viscosifier	Drilling Specialties
HE 150	AMPS co-polymer	Viscosifier	Drilling Specialties
HE 300	AMPS co-polymer	Viscosifier	Drilling Specialties
HE 400	AMPS co-polymer	Viscosifier	Drilling Specialties
Hostadrill 4706	Vinyl amide/vinyl sulfonated polymerase	Fluid Loss	Clariant
Flodrill PAS 50	Partially hydrolysed polyacrylamide (PHPA)	Viscosifier	SNF
Thermacheck	Vinyl amide/vinyl sulfonate co-polymer	Fluid Loss	BAROID
Thermacheck LV	Vinyl amide/vinyl sulfonate co-polymer	Fluid Loss	BAROID

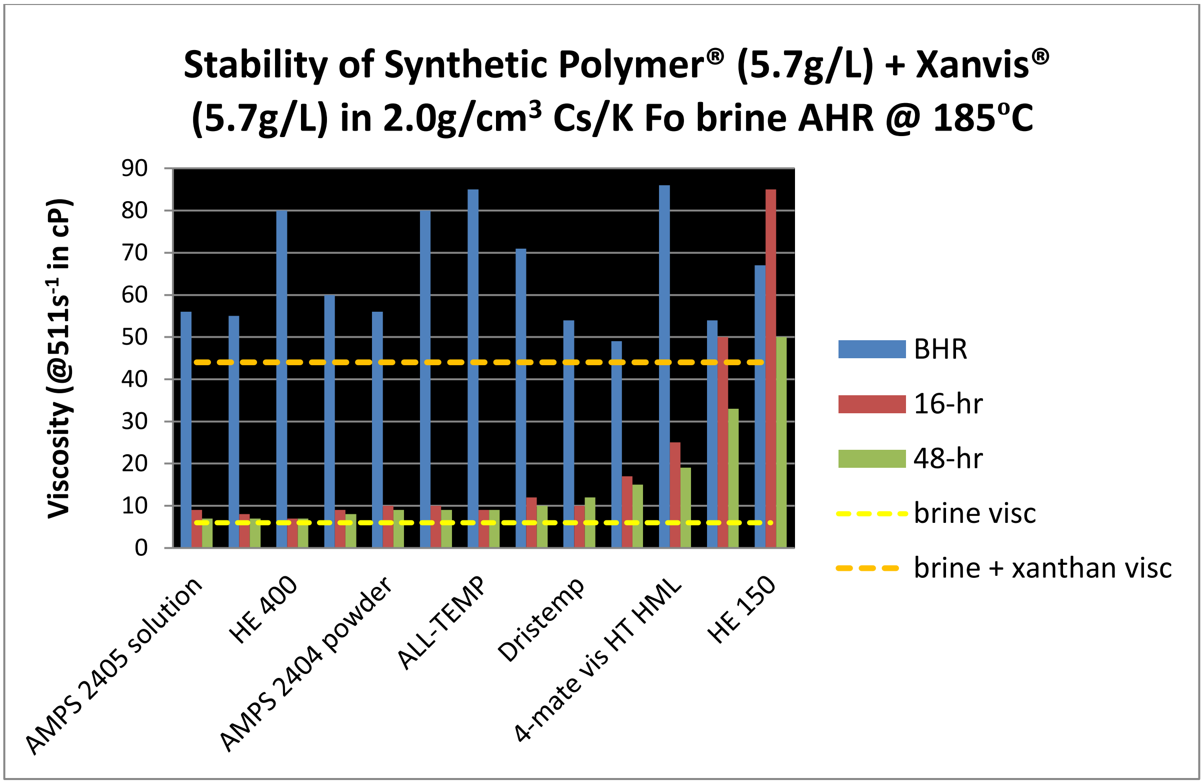


Figure 3.33 *16- and 48-hr dynamic ageing of various synthetic products and xanthan in a 2.0g/cm^3 Cs/K formate standard blend @ 185ºC (Rheologies were measured @ 50ºC as a standard, dotted yellow line represents base brine viscosity)*

Generally, synthetic polymers are notoriously difficult to hydrate in high concentrated formate brines, without significant energy from heat primarily. Therefore, xanthan was added in concentrations of 5.7g/L along with the same concentration of synthetic polymer as to ensure any un-hydrated synthetic material remained homogenous in solution when distributing between cells for dynamic ageing – thus the "two phase" system emerges. The viscosity of 5.7g/L xanthan in 2.0g/cm^3 Cs/K formate is 44cP before dynamic ageing or BHR (**orange** dotted line); so any additional rheology is a result of the synthetic polymer partially hydrating in solution. As it is already known from section **3.3.3**, that xanthan gum will have completely degraded after 16 hours at 185ºC, so the resulting viscosity should be purely a result of synthetic material.

Figure 3.33 illustrates a sizable distribution between the effectiveness of synthetic polymers in 2.0g/cm^3 Cs/K formate; with few products demonstrating their competency as potential HPHT viscosifiers at 185ºC. The HE100 and HE150 "hostile environment" polymers appear to be the most stable with regards to viscosity after 16 and 48 hours dynamic ageing. Interestingly, HE300 and HE400 were designed to be more robust than the 100 & 150 series, but they are incompatible in 2.0g/cm^3 Cs/K formate, as they clump together (see **Figure 3.34 left**) to provide little to no viscosity in solution. Perhaps the high ionic nature of the brine is too great for the complexity of the polymer so it fails to hydrate – even after long term heating at HPHT temperatures. Also, as demonstrated in section **3.2.7**; it may be the buffer and high pH inhibiting polymer hydration so lowering pH may quite possibly give very different results.

Often, there is a limit to the positive effect of advanced polymer hydrolysis because if the degree of modification is too high, the polymer may become over sensitive to the salinity and/or hardness of the brine (Wever, Picchioni and Broekhuis 2011). This type of negative reaction has been observed in formates before, with another synthetic polymer; Driscal D® from Drilling Specialties (see **Figure 3.34 right**). This coincidentally was designed as an improvement to Dristemp® - which functions extremely well in Cs/K formate as a fluid loss additive but it does not exhibit great viscosity, according to **Figure 3.33**. Auerbach, 1985 recognized a similar issue with partially hydrolysed polyacrylamide (PHPA), where the presence of excess salt in solution causes the polymer to collapse into a tight ball with a low hydrodynamic volume and thus, reduced solution viscosity (Auerbach 1985). This finding is in general agreement with results in **Figure 3.33**, as PHPA didn't seem to hydrate initially – looking at the BHR data; but did provide some viscosity after dynamic ageing.

Figure 3.34 *2.0g/cm^3 Cs/K formate and 5.7g/L HE300 (left) and Driscal D (right) Polymer "ball" after dynamic ageing for 16 hours @ 185ºC*

3.4.2 HPHT Viscosity Analysis of Best Performing Synthetic Materials

For further analysis of the best synthetic polymers; the Haake MARS III pressure cell was utilized to obtain the full viscosity profile over 48 hours at a similar shear rate of 500s^{-1} @185ºC with ~20+ bar pressure applied (to inhibit sample boiling).

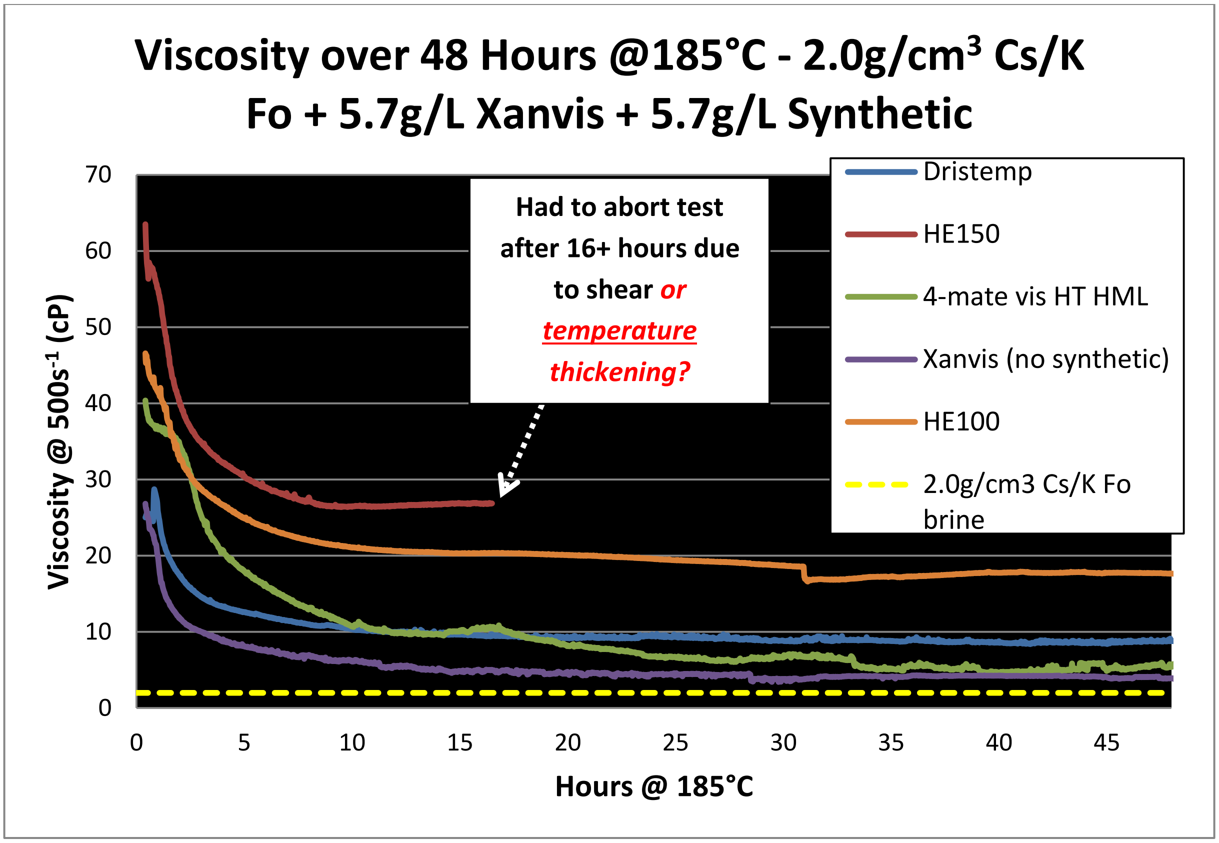


Figure 3.35 *MARS III HPHT viscosity data over 48 hours @ 185ºC (2.0g/cm3 Cs/K formate brine viscosity is ~2cP at 185ºC)*

The data measured from the HPHT rheometer (**Figure 3.35**) appears to be consistent with dynamic ageing results as the HE® polymers demonstrate excellent stability over 48 hours compared to the rest of the synthetics. It is not feasible to compare values directly, as the HPHT rheometer is measuring "real-time" viscosity at $500s^{-1}$ (185ºC) continuously over 48 hours, and the dynamic ageing tests evaluate the degradation (or recovery) from extreme temperatures using the Fann35 viscometer at $511s^{-1}$ at 50ºC. However, a similar trend in stability for both can be observed. For example, the 4-mate Vis HT HML illustrates progressive degradation over time which is evident in both sets of results (**Figures 3.33 & 3.35**). In addition, fluid loss polymer Dristemp demonstrates a stable rheology over 48 hours with no signs of decomposition, indicating that it should still be "active" with regards to fluid loss. It is important to remember that these tests are designed to solely evaluate viscosity, so they may not truly represent a polymer's genuine ability as a drilling fluid additive – as many of the synthetics listed were designed for fluid loss control and not viscosifying power (i.e. Dristemp, Thermacheck Regular and LV).

To confirm that the enhanced thermal stability of these synthetic polymers in **Figure 3.35** is solely contributed to the high concentration of formate salt protecting the synthetic material at high temperatures; Anderson 2013, repeated dynamic ageing tests similar to section **3.4.1** using water as the base fluid as well as a substantially lower concentrated Cs/K formate brine (5.6mol/L). As a result, all best performing polymers; Dristemp, 4-mate vis HT HML, HE100 and HE150 degraded almost completely after just 16 hours at 185ºC in both pure water and the lower concentrated formate analogue. However, viscosities before dynamic ageing were higher indicating that synthetic materials were more able to hydrate in aqueous and lower concentrated solutions (Anderson 2013). These elusive findings again, clearly illustrate the importance and respective value of maintaining a high concentration of formate salt in solution, with regards to polymer stabilization.

Through further evaluation of the MARS III data and dynamic ageing tests, it was discovered that the HE® polymers exhibit very different physical behaviour with regards to rheology. HE100 demonstrated shear thinning characteristics in the Fann35 viscometer, obtaining a lower apparent viscosity at higher shear rates, whereas HE150 showed slight shear thickening behaviour after 48 hours with the viscosity at 1022s^{-1} shear rate being higher than at 511s^{-1} (see **Figure 3.36**). Occasionally, it has been reported that an increase in the degree of polymer hydrolysis for example; the modification from HE100 to HE150 during production can lead to an onset of shear thickening behaviour depending on the solute and polymer concentration (Wever, Picchioni and Broekhuis 2011). The shear thickening effect for HE150 was potentially further identified in the MARS III pressure cell (see **Figure 3.35**) as the test had to be aborted after ~16 hours as the rotor had overheated – the same test was repeated three times with the same occurrence. Therefore, it is entirely possible that the progressive thickening of the fluid at 500s^{-1} may have caused this unusual operating fault. With that said, it could instead have been the <u>temperature</u> thickening effect of the HE150 polymer that caused the rheometer to break; thus the same fluid should be re-tested at lower shear rates to confirm whether the effect is shear or temperature thickening.

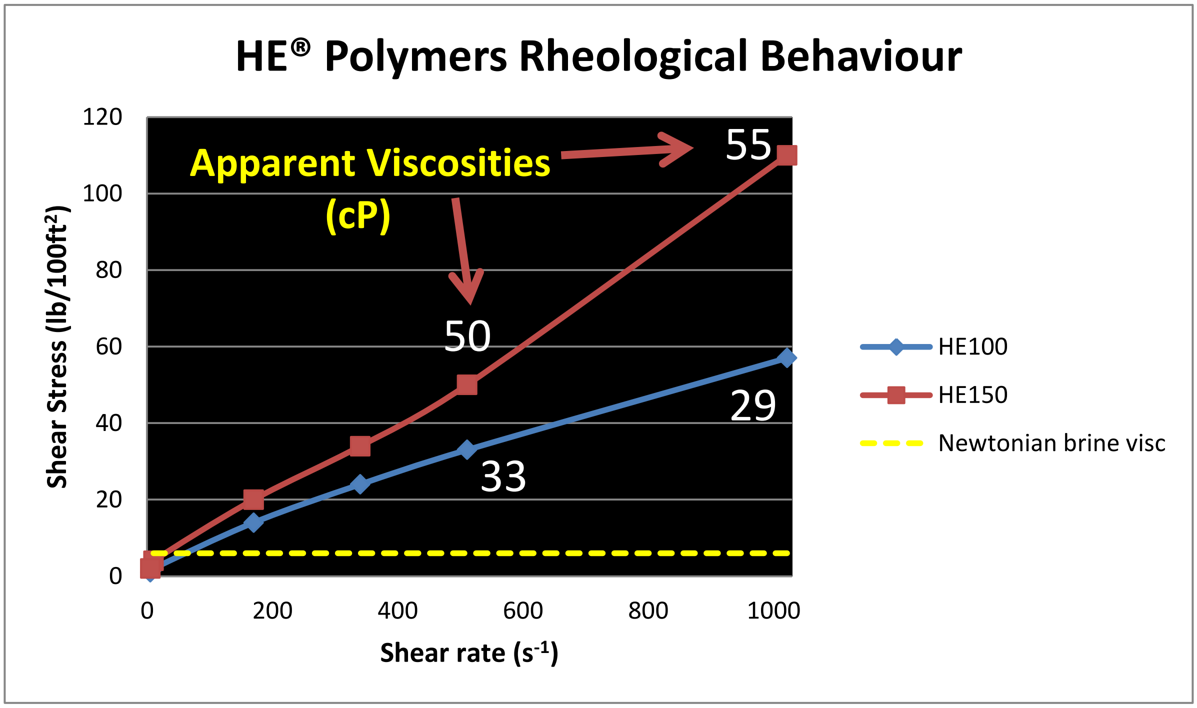


Figure 3.36 *Shear thinning effect of HE100 vs. shear thickening effect of HE150 polymer with Xanvis in 2.0g/cm*^{3} *Cs/K formate after dynamic ageing for 48 hours @ 185ºC*

Shear thickening behaviour can occur for certain polymers above a given shear rate (between 500-1000s^{-1} in this instance), as intramolecular associations such as hydrogen bonds are broken which extends the polymer chain, to promote stronger interchain polymer synergy and thus increased viscosity. For a pseudoplastic fluid (shear thinning), the application of shear disrupts both intra and interchain associations which leads to a reduction in solution viscosity (Wever, Picchioni and Broekhuis 2011). With that said, a shear thickening polymer is completely inappropriate for use in drilling fluids, where high shear is applied in order to drill faster with a lower viscosity fluid – so HE150 may not be suitable for certain applications.

3.4.3 Long Term Polymer Stability Tests

Due to today's advanced field applications, the operators demand for fluids that can withstand long-term high temperature requirements is increasing. With this in mind, the best performing polymers were dynamically aged for two weeks at 185ºC to investigate their suitability in 2.0g/cm^3 Cs/K formate for longer term hostile conditions.

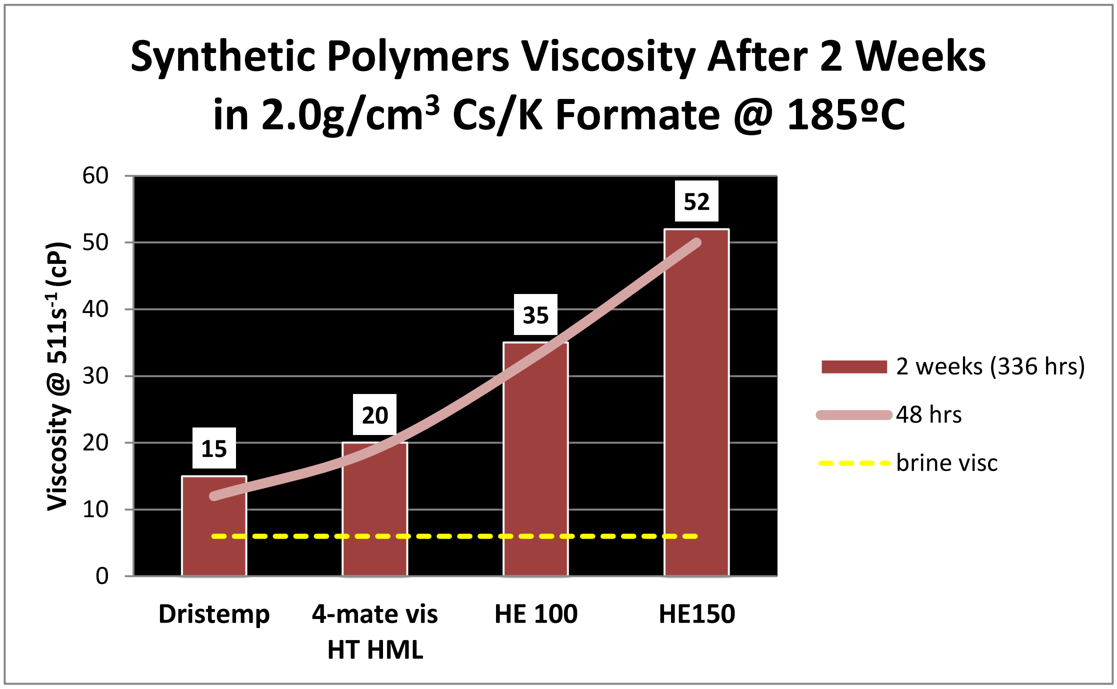


Figure 3.37 *Viscosity of 5.7g/L Xanvis® and synthetic polymer (5.7g/L) in 2.0g/cm^3 Cs/K formate brine after 2 weeks of hot-rolling at 185ºC (yellow dotted line = 2.0g/cm^3 Cs/K formate brine viscosity is ~6cP at 185ºC)*

Surprisingly, **Figure 3.37** demonstrates that synthetic polymers in fact show increased stability after two weeks at 185ºC, compared to after 48 hours so their ability to remain operational in HPHT environments is undoubtedly impressive. The enhancement in viscosity of each fluid after 14 days exposure to 185ºC suggests that the synthetic material is still hydrating and could potentially remain stable at this temperature for a further 3-4 weeks before degradation occurs. Moreover, **Figure 3.37** provides encouraging data for hypothesizing the stability of certain synthetic polymers at even higher temperatures in the 2.0g/cm^3 Cs/K formate blend, particularly with the HE® series 100&150.

3.4.4 Evaluation of HE® Polymers in Formate Brines

The HE® (Hostile Environment) high molecular weight synthetic polymers were developed by Chevron Phillips Chemicals for use in completion, work over and stimulation applications. A number of desirable properties such as solubility in a wide variety of brines (namely the halides i.e. chlorides and bromides), with increased resistance to shear degradation and excellent thermal stability were targeted during the manufacturing process. However, during initial application of HE150 in acidizing treatments it was recognized to provide excellent friction reducing properties at very low polymer concentrations – drag reduction up to 84% in straight pipe and 69% in coiled tubing when dispersed at 0.17g/L in fresh water. In the heavier brines, slightly higher polymer concentrations were required to achieve similar results. Further, HE150 was successfully used in the field for coiled tubing applications in the Haynesville Shale, North Louisiana producing significantly better friction reduction than conventional additives, with lower chemical loadings (Fox, Stouffer and Utley 2008; Fox and Bainum 2010). Thus, it is stimulating to add "proven stability in highly concentrated formate brines at HPHT conditions over a period of 14 days" to the HE® Polymers 100 &150's credentials list, due to the undertaking of this novel research.

After initial qualification and long term stability tests, it was decided to focus on evaluating stability limits for HE® polymers 100 & 150 as they seem to be by far the most robust additives in terms of viscosity control. Using the same concentrations as before (5.7g/L), HE® polymers and xanthan were dynamically aged for 16-hrs at 205, 220 and 230ºC.

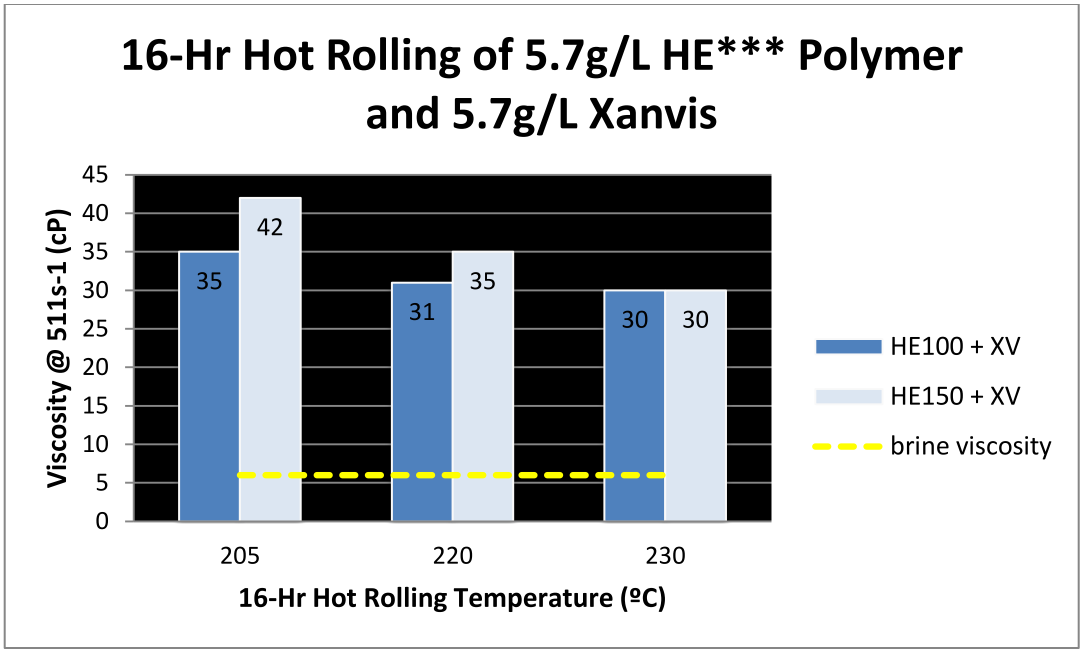


Figure 3.38 *16-hr stability of HE® polymers and xanthan in 2.0g/cm3 Cs/K formate brine (Newtonian brine viscosity of 2.0g/cm^3 Cs/K formate is 6cP @ 50ºC) at 205, 220 and 230ºC*

Results from **Figure 3.38** demonstrate that HE® polymers, 100 & 150 are inherently stable after dynamic ageing at ultra-HTHP temperatures at relatively low concentrations (5.7g/L) which outperforms any other viscosifying agents previously tested for use in formate drilling fluids. Since the hot-rolling ovens for dynamic ageing are only suitable for temperatures below 232ºC, the MARS III HPHT rheometer was utilized to gain more information on the HE® polymers behaviour above this temperature, i.e. 250ºC.

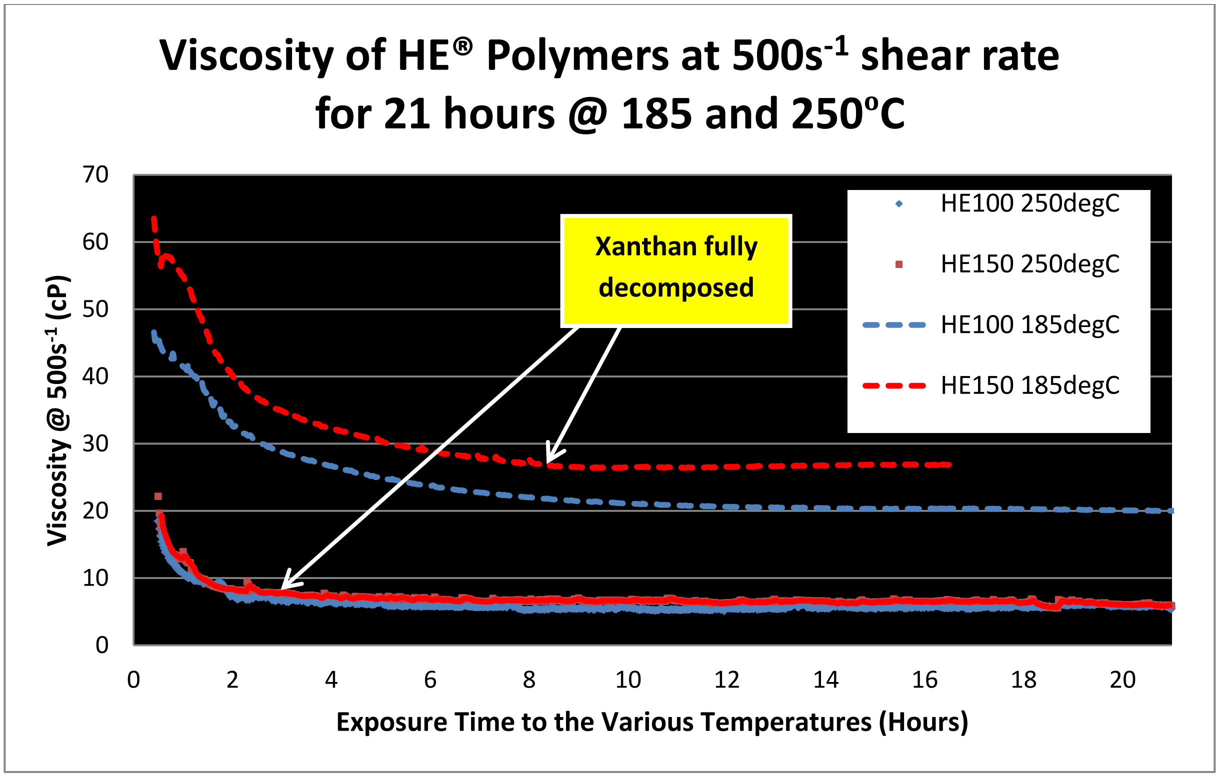


Figure 3.39 *MARS III HPHT viscosity data of 5.7g/L Xanvis and 5.7g/L HE® Polymer in 2.0g/cm3 Cs/K formate over 21 hours @ 185 and 250ºC*

As expected, viscosities of HE® polymers are much lower at 250ºC than at 185ºC due to the thermal thinning effect at higher temperatures. However, it is encouraging to observe that rheology is generally stable for both polymers at 250ºC after the initial drop at 2 hours, according to **Figure 3.39** - this is highly likely to be the xanthan quickly degrading. In fact, it is possible to estimate on **Figure 3.39** the duration for which xanthan gum fully decomposes at each temperature - as it's the same decline in both HE100 and HE150 polymers (i.e. ~10 hours @ 185ºC and ~3 hours @ 250ºC). Since HE® polymers do not hydrate in solution before heating, it is necessary for the xanthan to be present in the formulation for homogeneity at low temperatures. Therefore, the fluid provides a "two-phase" polymer system where xanthan gum implements initial suspension properties but the synthetic material assumes viscosity as it begins to hydrate when the sacrificial biopolymer; xanthan degrades. Fox *et al.*, 2008 stipulated that the HE® polymers are normally sheared into liquid glycol ether initially, for ease of dispersion and to avoid "lumping" in the brine so perhaps alternative hydration techniques are necessary if not combined with xanthan or other viscosifiers in the field (Fox, Stouffer and Utley 2008). Further, Maresh, 2009 filed a patent claiming that a formate compound is not required to achieve high temperature fluid stability, as long as the fluid contained at least one polysaccharide and enough synthetic (or polyacrylamide) material to bond with the biopolymer such that it is less likely to bond with free oxygen or radicals at high temperatures. However, this only provided stability up to the range of 135-162ºC, making it completely irrelevant compared to discoveries made in the present study with a system composed of a formate compound, polysaccharide and AMPS containing synthetic material which is stable at temperatures in excess of 250ºC (Maresh 2009).

To evaluate the recovery of HE® polymers after exposure to 250ºC for 21 hours; shear rate vs. viscosity profiles were measured at 50ºC to compare with fresh samples not previously exposed to temperature (BHR). The "Xanthan BHR" **yellow** line is solely 5.7g/L Xanvis in 2.0g/cm^3 Cs/K formate brine for control measures. Though, before even considering the effect of temperature on the fluid, it is evident from **Figure 3.40** that the HE® polymers provide a synergistic effect when administered with xanthan as they do not provide viscosity individually in the 2.0g/cm3 Cs/K formate brine, albeit their contribution makes the fluid notably less shear thinning.

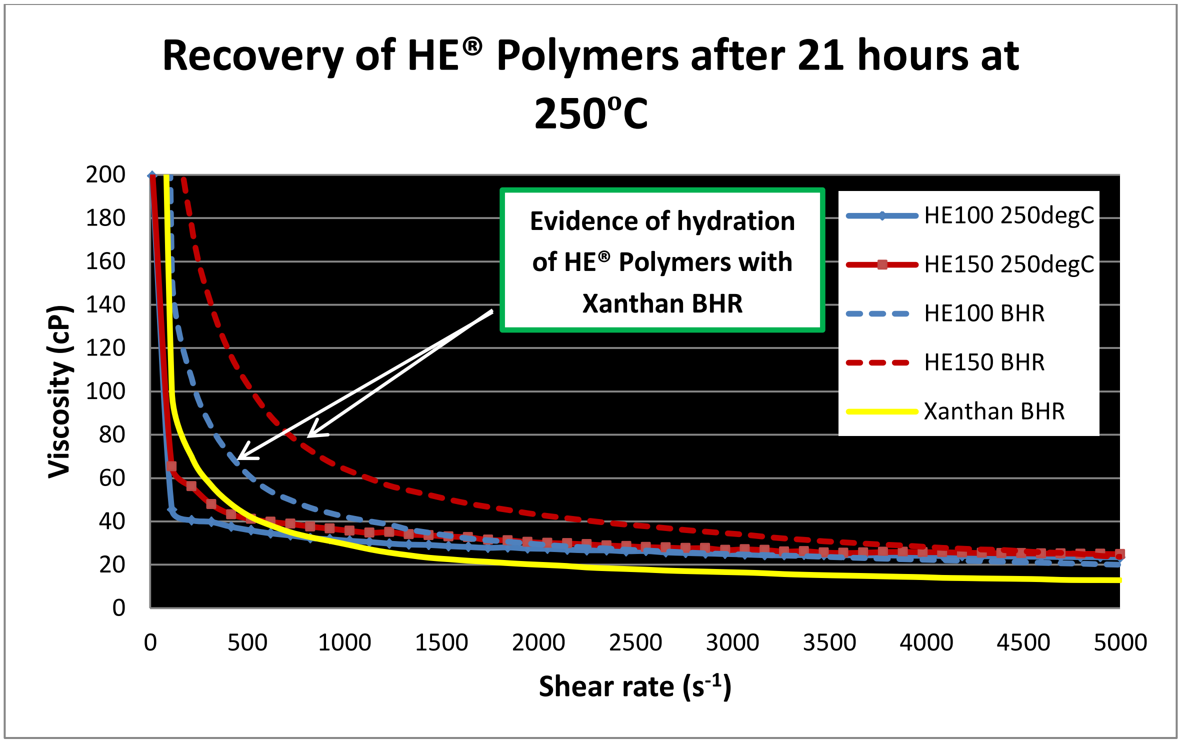


Figure 3.40 *Rheology of HE® Polymers (5.7g/L) with xanthan (5.7g/L) after 21 hours at 250ºC (data measured at 50ºC)*

Using **Figure 3.40**, it is difficult to analyse the degree of polymer decomposition as the distribution of shear rate is so widely spread; however it is clear from observing the data that HE® polymers are still very much “active” retaining a 300rpm/511s^{-1} viscosity value of 35 and 41cP @ 50ºC for HE100 and 150 respectively, even without xanthan’s initial contribution (see **Table 3.13**).

Table 3.13 Degradation of HE® Polymers and Xanvis after 21 hours at 250ºC (511s^{-1} shear rate)

HE® Polymer	**Viscosity of Control or BHR fluid (cP)**	**Viscosity after 21 hours at 250ºC (cP)**	**Viscosity Decrease (%)**
100	60	35	42
150	100	41	61

Therefore, the viscosity decrease (%) could solely be result of the degradation of xanthan gum so these values are not truly representative of the synthetic polymers state of efficacy. To investigate exclusively the recovery of synthetic polymers; 5.7g/L HE® series in 2.0g/cm^3 Cs/K formate solutions were prepared without xanthan and dynamically aged at 120ºC to induce polymer hydration. Rheologies were measured at 50ºC on the MARS III rheometer and their contribution added to **Figure 3.40**. Since the viscous characteristics of most polymers are far more pronounced at the lower shear rates (<300s^{-1}), the graph was adjusted to focus on the viscosities at lower shear rates, or low shear rate viscosity (LSRV) (**Figure 3.41**).

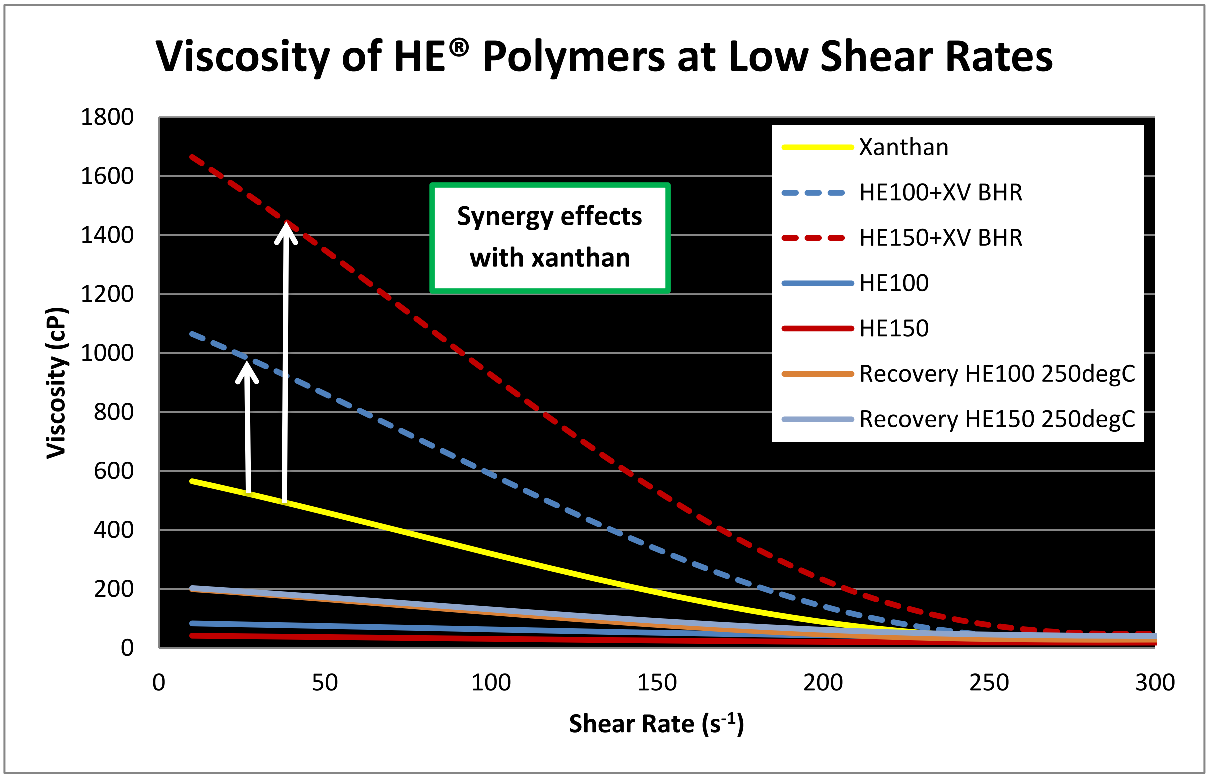


Figure 3.41 *Difference in viscosities of HE® polymers and xanthan at LSRV before and after 21 hours exposure to 250ºC*

Again, **Figure 3.41** demonstrates the clear synergistic effects between xanthan gum and the HE® polymers before heat exposure at LSRV, most notably with HE150. However, as xanthan degrades completely after a few hours at 250ºC (as observed in **Figure 3.39**), the recovery viscosities of both synthetics exhibit a similar rheology. This implies that HE100 is more thermally stable, as its activity is the least varied according to **Figure 3.41** and degradation characteristics in **Table 3.13**. This recommendation is corroborated with additional dynamic ageing tests using the same polymer system in Cs/K formate from Anderson, 2013 (Anderson 2013). Also, measuring viscosities of HE® polymers without xanthan "HE100 & HE150" (see **Figure 3.41**) has confirmed the obvious synergy between synthetic material and xanthan gum, as they have a much lower viscosity than even the recovery fluid (with xanthan completely degraded after 21 hours at 250ºC). It is likely that the HE® polymers had not fully hydrated (without xanthan) at 120ºC and a higher temperature is required in order to "activate" their viscosifying effects. Most importantly, as observed in **Figure 3.37** with the long term dynamic ageing tests, the synthetic materials could still be hydrating in this ultra-HTHP environment protected by the Cs/K formate brine. Since these incredible synthetics have illustrated little degradation after 21 hours 250ºC, it was decided to test their performance at 300ºC – the absolute temperature limit of the MARS III HPHT rheometer. However, due to problems with the temperature sensor, the rheometer was unable to reach these temperatures and further technical assistance is required. This should be given high priority in further work to characterize the temperature ceiling of robust HE® polymers in Cs/K formate brine once the HPHT rheometer is back to operating conditions.

Since the MARS III rheometer was temporarily "out of order," the highest rated static oven can reach 250ºC, so fluids were statically aged for 16-72 hours to monitor any further degradation at 250ºC.

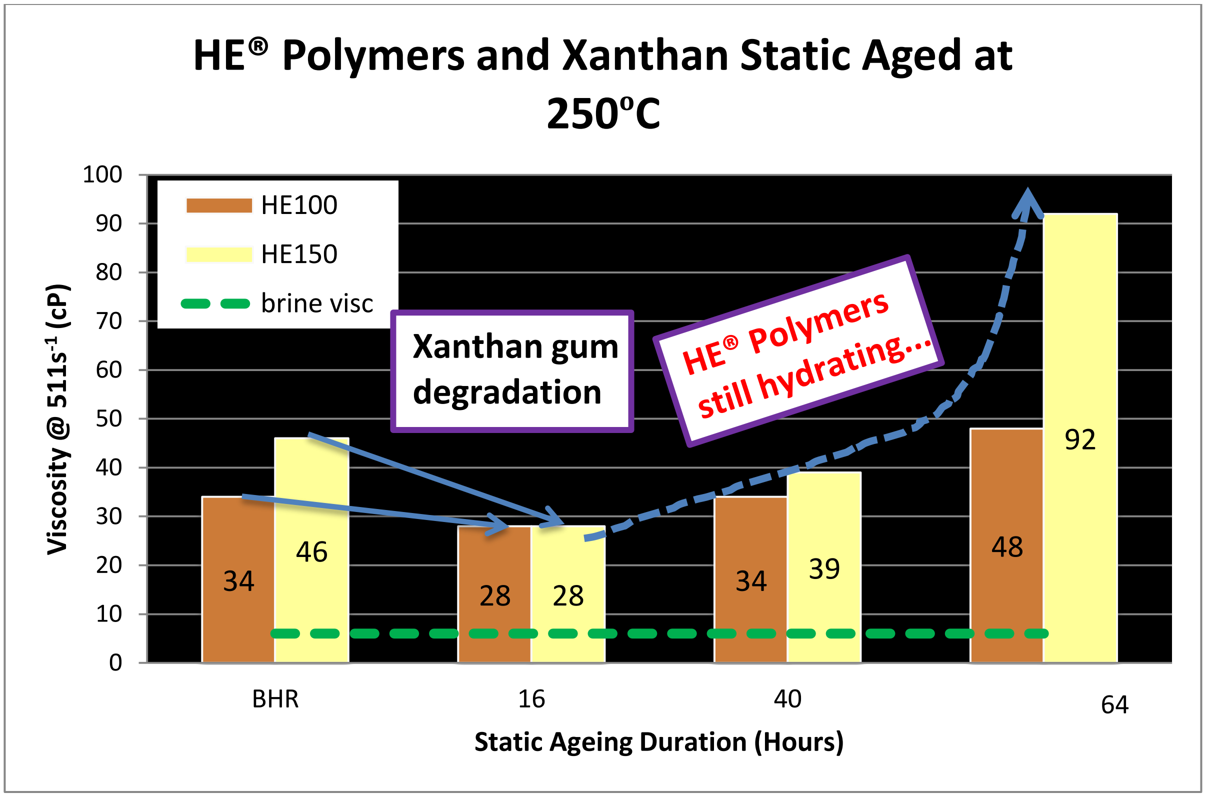


Figure 3.42 *Viscosities of 5.7g/L HE® polymer and xanthan after static ageing @ 250ºC for varying time periods to monitor any degradation (pH dropped to around 9 after 64 hours)*

Results from static ageing at 250ºC are fascinating in terms of the temperature endurance and reliability of HE® polymers in 2.0g/cm^3 Cs/K formate – the longer duration exposed to 250ºC, the further viscosity builds, according to **Figure 3.42**. After 16 hours ageing, viscosity initially drops due to the degradation of xanthan gum affecting the HE® polymers hydration. But, after 16 hours the viscosifying power begins to slowly "kick-in" or hydrate which only becomes stronger over time (see **Figure 3.42**). If this staggering degree of stability is observed at 250ºC, then it is stimulating to hypothesize the potential temperature ceiling of such enduring synthetic polymers in Cs/K formate brine. Already, it appears as though they may introduce exciting new prospects for highly concentrated formate systems in ultra and potentially extreme HPHT operations which will be discussed further in Conclusions and Future work.

In terms of the “two-phase” polymer structure at these temperatures, it was evident that xanthan gum had completely degraded into solid material which stuck to the side of the hot-rolling cell (see **Figure 3.43**). This is a clear reminder that creating a formate drilling fluid at 250ºC would be an extremely challenging process or may not be possible, with regards to maintaining fluid loss control etc. as most other additives are not nearly as robust. Be that as it may, HE® polymers could be utilized with Cs/K formate as high density, ultra-HPHT temperature completion or work over fluids e.g. fracturing or LCM pills. The fact that these synthetic polymers do not yield straight away until triggered by high temperature could be a potential advantage, as the fluid could be pumped easier and would only become “activated” down hole.

Figure 3.43 *Mineralized xanthan gum in hot-rolling cell after dynamic ageing for 64 hours @ 250ºC (Photograph taken in CSF Laboratory)*

Static ageing tests do not subject the fluid to constant mechanical shear or “rolling” as with the other tests at high temperature so a slightly different rheological profile may occur. However, HE150 does not show any shear thickening behaviour after static/dynamic ageing or testing in the HPHT rheometer at temperatures above 185ºC (**Figure 3.36**). Perhaps the excessive temperatures inhibit the onset of shear thickening, thus creating a more appropriate balance of inter and intramolecular bonding between the polymer chains. Still, for use in a drilling or completion fluid, the concentrations of HE® polymers (especially

HE150) would need to be closely monitored and controlled as it is undesirable for fluid properties to change so drastically over prolonged heating. In this respect, HE100 is still the preferred synthetic additive. Careful fluid design can improve these properties which can be achieved through extensive formulation work to meet the prospective specifications.

Moreover, it is essential to reiterate that a 2.0g/cm^3 Cs/K formate is definitely not the best choice of brine for stabilizing polymers and stability could increase substantially using saturated potassium formate as the base fluid (section **3.3.3**). Further, if a higher density is required; a 2.0g/cm^3 Cs/K formate standard blend could be increased to a 2.1g/cm^3 non-standard blend or thereof etc. to enhance stabilization by increasing the overall formate molar concentration (section **3.3.4**). Thus, having already established a temperature stability for HE® polymers in excess of 250ºC in a suboptimum formate brine without any additional stabilizing chemistries, it is exciting to consider the potential temperature endurance of these polymers through further manipulation of the formate base.

Since the exact chemistries of these HE® polymers is not known because of confidentiality issues with the suppliers, it is difficult to understand the mechanisms by which they resist decomposition in formate brines to such high temperatures. The small amount of information available is that they are based on variations of the AMPS monomer (2-acrylamide-2-methylpropanesulfonic acid sodium salt). The AMPS monomer is normally added to the main chain of the polymer backbone to improve salt tolerance as the strongly hydrophilic –SO_3H group improves electrostatic repulsion and increases water solubility. The large side group of AMPS, also significantly reduces hydrolysis of the main polymer backbone at high temperatures due to the steric effect inhibiting polymer coiling/folding (Wu et al. 2012). In addition, Ezell *et al*. 2008 recommend using synthetic polymers modified with extremely hydrophilic monomers such as AMPS, as opposed to hydrophobic monomers in dense electrolyte rich brines so perhaps this is the key to the success of the less complicated HE® series polymers i.e. 100 & 150, as opposed to 300 & 400 (Ezell et al. 2010). However, in the literature there are many contradictory statements made to explain the enhanced stability of polymers using highly concentrated salts in solution. For this reason, it is impossible to compose realistic assumptions about the exact stabilizing mechanism of HE® synthetic polymers in 2.0g/cm^3 Cs/K formate brine without knowing more about their generic chemistries.

Chapter 4 : Conclusions and Further work

4.1 Conclusion

This novel research has identified a number of distinguishing characteristics about the activity of polymers in formate brines, which has altered the understanding and future approach to increasing viscosity and maintaining stability at extreme temperatures in high salt concentrated polymer solutions. Contrary to popular belief, this research has shown that the viscosity of most biopolymers and xanthan gum actually increase in highly dense salt solutions, such as the formates after the critical concentration of polymer has been exceeded (in this case <8.57g/L). Generally, the polymer viscosity develops with increasing formate salt concentration and decreasing water activity so the mindset that polymers cannot yield in the absence of water is completely misguided on this occasion. The mechanism to which formate salts increase the viscosity of polysaccharide solutions is predicted to be through enhanced intra and intermolecular hydrogen bonding which increases the overall molecular weight of polymer. The increased interaction is promoted as a result of lack of “free space” in solution and possibly suppression of electrostatic associations, which allows individual polymer chains to come into much closer contact with one another, due to lack of ionic repulsion.

This research has also shown that only xanthan gum can hydrate sufficiently at natural pH (10) in buffered formate brines, where other biopolymers i.e. welan, guar, and CM guar struggle with this level of alkalinity and require the pH to be lowered in order to increase viscosity properties. Since most of the biopolymers exhibit higher viscosities at the same pH (7) in concentrated formate brines than in pure water, then it is decidedly not the extreme saline environment affecting hydration properties, but more the high alkaline pH or buffer. This is a significant discovery with regards to polymer behaviour in formate brines, as the reluctance of polymers to yield was formerly thought to be attributed to the mass concentrations of salt dissolved in solution and lack of “free water” for hydration. Furthermore, the biopolymer scleroglucan was found to be completely ineffective in high concentrated formate brines at any pH, whereas previous literature had suggested it had been compatible (Howard 2009), but only in extremely low concentrations of formate salt (Gallino et al. 1996).

Also in contradiction to the literature; results confirm that the physical presence of carbonate/bicarbonate can have a detrimental effect to the viscosity and T_m of xanthan gum in highly concentrated formate brines. It was found that increasing pH without the use of buffer considerably reduces solution viscosity (due to the suppression of intramolecular hydrogen bonding), but ultimately pH alone has little effect on the xanthan T_m in both caesium and potassium formate solutions.

In general, the temperature stability of xanthan gum and other biopolymers in concentrated formate brines can be optimized by increasing formate molar concentration in the same manner as with increasing viscosity. Moreover, the formate ion is a strong kosmotrope or "water-structuring" anion that demonstrates stabilizing and salting-out effects on proteins and polymer macromolecules (Zhang and Cremer 2006). The present study has confirmed that; the order of stabilizing effects of individual cations in formate solutions generally follows the Hofmeister series of cations; Li^+, Cs^+, Na^+, K^+ with the response becoming more pronounced at higher salt concentrations. Also, with regards to the formate blends; stability of polymers can be increased by losing water creating a more concentrated solution to increase the rigidity of main chain backbone, thus reducing the available sites for decomposition reactions to take place.

Additionally, the current caesium formate stock (2.20g/cm^3) has demonstrated significantly greater stability properties with regards to xanthan gum than previously documented in the Formate manual (Howard 2009). For example, the xanthan T_m in 2.20g/cm^3 caesium formate was 177ºC - a 20ºC increase from the T_m measured in earlier publications. This could potentially be contributed to the higher concentration of contaminants due to lower availability of "high grade" pollucite at the Tanco mine, or the slightly different measuring techniques.

Through initial biopolymer qualification testing, it has been confirmed that xanthan gum is by far the most stable biodegradable viscosifier for use in formate drilling and completion fluids, also in terms of ease of use as it can still hydrate without having to lower pH to neutral. With regards to evaluating different thermal stabilizer products; an optimized combination of 5% polyethylene glycol (200 g/mol) and 5.7g/L magnesium oxide were found to react synergistically to inhibit xanthan degradation in potassium formate up to 200ºC for 16 hours without the use of synthetic polymers. The saturated potassium formate brine (1.57g/cm^3) had no carbonate/bicarbonate present, however since magnesium oxide is a natural buffer, it ensured pH remained above 10 even after dynamic ageing at 200ºC.

Through a lengthy characterization process of various synthetic polymers in 2.0g/cm^3 Cs/K formate brine; two successive polymers have prevailed. HE® polymers 100 & 150 series from Drilling Specialties have exhibited proven stability over 64 hours at 250ºC with their viscosities actually increasing with the prolonged exposure time, being crucially protected by the high concentration of formate salt in solution. With superior HPHT laboratory measuring techniques, it is predicted that HE® polymers will remain stable at temperatures over 280ºC.

Although HE® polymers have impressed so far by their ultra and potentially extreme HPHT stability measures, they suffer hydration difficulties initially in the formate brine unless combined with suspending agent; xanthan gum. In fact, biopolymer and synthetic material impart synergistic effects before any heat exposure as they produce a substantially higher rheology combined than administered at the same concentration individually. Thus, a "two-phase" polymer system is created to maintain a stable viscosity through various temperatures the fluid may experience in the field.

Due to conclusions drawn from the present study, the understanding of natural and synthetic polymer behaviour in formate brines has transformed from the prior "trial and error" approach, into generating more educated decisions as how to achieve desired viscosity specifications with the corresponding base brine.

4.2 Further work

Engineering a good HPHT drilling fluid is about managing an appropriate balance between individual additives to support each other’s specific functions. The luxury of working with formate drilling fluids is that generally there are only two properties required of the additives; viscosity and fluid loss control, which makes formulating formate muds a lot simpler. This is due to the fact that the base formate brine fulfils the rest of the desired mud characteristics for example; density, lubricity, biocide, shale inhibition, corrosion inhibitor, alkalinity, polymer stabilizer etc. which are normally obtained from additional products. Therefore, it is especially relevant to further study the synergy effects between successful polymers and products e.g. xanthan gum, HE® polymers, MagOx, and PEG and utilize these in future mud formulations.

In order to incorporate new successive polymers/additives into the original mud composition for higher temperature application, it is highly recommended to monitor their effects individually on the standard products and ensure their natural synergy with one another is not influenced by the new synthetic additions. Also of utmost importance; is that the optimal concentration of additives is determined for maximum effectiveness. In addition, a significant challenge with regards to creating a formate drilling mud; is the fluid loss concern which has not been investigated during the course of this research. Therefore, laboratory resources must be utilized towards the development of fluid loss additives which can withstand similar ultra-HPHT temperatures as the extremely robust HE® polymers.

In terms of the alkalinity effect on polymers, more laboratory research is required to suitably understand the relationship between pH and buffer in optimizing hydration and stability effects in full mud formulations and also in synthetic polymers. Further, magnesium oxide can be employed as an alternative buffer for formate drilling fluids; to develop improved hydration techniques for other biopolymers which do not hydrate at high pH with carbonate/bicarbonate present for example, welan gum.

With regards to stabilizing additives, dynamic ageing tests have proved that certain additives inhibit the thermal degradation of xanthan a lot more than others. Therefore, it would be interesting to measure T_m of xanthan combined with most successful products to gain a better understanding of their stabilizing mechanism.

As a result of synthetic polymer characterization, HE® polymers from Drilling Specialties have shown outstanding resistance to degradation in $2.0g/cm^3$ Cs/K formate brine to the extent where the measuring equipment is not suitable for such adverse testing environments. To identify these polymers true temperature potential, an improved pressure cell for the MARS III must be implemented, since the current device cannot satisfy the demand of extreme HPHT testing. For this reason, it is compelling to envisage the potential high density field applications that formate fluids may be considered for in the growing ultra and extreme HPHT market, seeing as previous utility of formate brine <u>and</u> polymer has never exceeded 200ºC (Messler et al. 2004).

Chapter 5 : References

ANDERSON, Z., 2013. *Environmentally friendly XHPHT drilling fluid.* Unpublished MSc thesis, Robert Gordon University.

APALEKE, A.S., AL-MAJED, A.A. and HOSSAIN, M.E., 2012. *Drilling Fluid: State of The Art and Future Trend.* Cairo, Egypt: Society of Petroleum Engineers.

ASH, G.S., CLARKE-STURMAN, A.J., CALVERT, R. and NISBET, M.T. 1983. Chemical Stability of Biopolymer Solutions. *SPE Annual Technical Conference and Exhibition.* 5-8 October 1983. San Francisco, California: 1983 Copyright 1983 Society of Petroleum Engineers.

AUERBACH, H.M., 1985. Prediction of Viscosity for Xanthan Solutions in Brines. *SPE Oilfield and Geothermal Chemistry Symposium.* 9-11 March 1985. Phoenix, Arizona: 1985.

BAKER, R., 2001. *A Primer of Oil-well Drilling: A Basic Text of Oil-well Drilling*. 6th Edition. University of Austin: Texas, USA.

BERG, P.C. et al., 2007. *Drilling, Completion, and Openhole Formation Evaluation of High-Angle HPHT Wells in High-Density Cesium Formate Brine: The Kvitebjorn Experience, 2004-2006.* Amsterdam, The Netherlands: SPE/IADC Drilling Conference.

BLACK, A.D. et al., 2008. *Optimization of Deep Drilling Performance With Improvements in Drill Bit and Drilling Fluid Design.* Orlando, Florida, USA: 2008, IADC/SPE Drilling Conference.

BRIGAND, G., 1993. CHAPTER 17 - SCLEROGLUCAN. In: JAMES N. BEMILLER and ROY L. WHISTLER, eds. *Industrial Gums (Third Edition).* London: Academic Press. pp. 461-474

BUNGERT, D., MAIKRANZ, S., SUNDERMANN, R., DOWNS, J., BENTON, W. and DICK, M.A., 2000. The Evolution and Application of Formate Brines in High-Temperature/High-Pressure Operations. *IADC/SPE Drilling Conference.* 23-25 February 2000. New Orleans, Louisiana: Copyright 2000, IADC/SPE Drilling Conference.

BYRNE, M., PATEY, I., GEORGE, L., DOWNS, J. and TURNER, J., 2002. Formate Brines: A Comprehensive Evaluation of Their Formation Damage Control Properties Under Realistic Reservoir Conditions. *International Symposium and Exhibition on Formation Damage Control.* 20-21 February 2002. Lafayette, Louisiana: Copyright 2002, Society of Petroleum Engineers Inc.

CAENN, R. and CHILLINGAR, G.V., 1996. Drilling fluids: State of the art. *Journal of Petroleum Science and Engineering,* 14(3–4), pp. 221-230

CAENN, R., DARLEY, H.C.H. and GRAY, G.R., 2011. *Composition and Properties of Drilling and Completion Fluids.* 6th ed. ed. US: Gulf Publishing Company.

DEYSARKAR, A.K., DADOO, A.P., et al. 2011. *High performance low residue guar for hydraulic fracturing and other applications.* United States US20110092696 A1.

DODI, G., HRITCU, D. and POPA, M.I., 2011. Carboxymethylation of Guar Gum: Synthesis and Characterization. *Cellulose Chemistry and Technology,* , pp. 171-176

DOWNS, J., 1991. High Temperature Thermal Stabilization of Xanthan in Drilling Fluids by the use of Formate Salts.

DOWNS, J.D., 2010. *A Review of the Impact of the Use of Formate Brines on the Economics of Deep Gas Field Development Projects.* Manama, Bahrain: Society of Petroleum Engineers.

EZELL, R. et al., 2010. *New Filtration-Control Polymer for Improved Brine-Based Reservoir Drilling-Fluids Performance at Temperatures in Excess of 400oF and High Pressure.* Lafayette, Louisiana, USA: Society of Petroleum Engineers.

FINK, J., 2011. *Petroleum Engineer's Guide to Oil Field Chemicals and Fluids.* Elsevier Science.

FOX, K.B., STOUFFER, C.E. and UTLEY, B., 2008. Evaluation of a New Friction Reducer for Brines. *American Association of Drilling Engineers.*

FOX, K.B. and BAINUM, M.S., 2010. *A New Synthetic Polymer Provides Improved Drag Reduction in Coiled-Tubing Operations in North Louisiana.* The Woodlands, Texas, USA: Society of Petroleum Engineers.

GALLINO, G., GUARNERI, A., POLI, G. and XIAO, L. 1996. Scleroglucan Biopolymer Enhances WBM Performances. *SPE Annual Technical Conference and Exhibition.* 6-9 October 1996. Denver, Colorado: 1996 Copyright 1996, Society of Petroleum Engineers, Inc.

GLASS, E.J., SOULES, A.D., AHMED, H., EGLAND-JONGEWAARD, S. and FERNANDO, R.H., 1983. Viscosity Stability of Aqueous Polysaccharide Solutions. *SPE California Regional Meeting.* 23-25 March 1983. Ventura, California: 1983 Copyright 1983 Society of Petroleum Engineers of AIME.

GARCÍA-OCHOA, F. et al., 2000. Xanthan gum: production, recovery, and properties. *Biotechnology Advances,* 18(7), pp. 549-579

GODWIN, JR.W., OGBONNA, J. and BONIFACE, O., 2011. *Advances in Mud Design and Challenges in HPHT Wells.* Abuja, Nigeria: Society of Petroleum Engineers.

GONZALES, J., QUINTAVALLA, R., BONAPACE, J. and VASQUEZ, J., 2013. Successful Field Implementation of a Novel Solids-Free System to Control Fluid Loss during Overbalanced Workover Operations in Southern Argentina. *2013 North Africa Technical Conference & Exhibition.* Apr 15 - 17, 2013 2013. InterContinental Citystar,Cairo, Egypt: 2013, Society of Petroleum Engineers.

HALLMAN, J.H. and BELLINGER, C.E., 2003. Potassium Formate Improves Shale Stability and Productivity in Underbalanced Drilling Operations. *CADE/CAO Drilling Conference, October 20-22, Calgary, Alberta, Canada., ,* pp. 1-8

HOLTSCLAW, J. and FUNKHOUSER, G.P., 2010. *A Crosslinkable Synthetic-Polymer System for High-Temperature Hydraulic-Fracturing Applications.*

HORTON, R.L. and PRASEK, B.B. 2009. *Methods and Compositions for Preventing High Density Well Completion Fluid Loss.* WO2009009343.

HOWARD, S.K., 1995. Formate Brines for Drilling and Completion: State of the Art. *SPE Annual Technical Conference and Exhibition.* 22-25 October 1995. Dallas, Texas: 1995 Copyright 1995, Society of Petroleum Engineers, Inc.

HOWARD, S., 2007. *Formate Manual, Section B2-1; Solubility of Gases in Formate Brines.* Version 1 ed. M.A. - USA: Cabot Corporation.

HOWARD, S., 2009. *Formate Manual, Section B5; Compatibility with Additives.* Version 2 ed. M.A. USA: Cabot Corporation.

HOWARD, S., 2010. *Formate Manual, Section A6: pH and Buffering.* Version 3 ed. M.A. U.S.A.: Cabot Corporation.

HOWARD, S., 2011a. *Formate Manual, Section A1; Chemistry.* Version 3 ed. M.A. USA: Cabot Corporation.

HOWARD, S., 2011b. *Formate Manual, Section A2; Brine Density and PVT Data.* Version 8 ed. M.A. USA: Cabot Corporation.

HOWARD, S. and DOWNS, J., 2005. Formate Fluids Optimize Production Rate. *AADE 2005 National Technical Conference and Exhibition*. 5-7 April, 2005. Houston, Texas, USA.

HOWARD, S.K. and DOWNS, J.D., 2009. *Formate Brines for HPHT Well Control—New Insights into the Role and Importance of the Carbonate/Bicarbonate Additive Package.* The Woodlands. Texas: Society of Petroleum Engineers.

KELLAND, M.A., 2009. *Production Chemicals for the Oil and Gas Industry.* 1st ed. Hoboken: CRC Press.

KULAWARDANA, E.U. et al., 2012. *Rheology and Transport of Improved EOR Polymers under Harsh Reservoir Conditions.* Tulsa, Oklahoma, USA: Society of Petroleum Engineers.

LEI, C. and CLARK, P.E., 2004. Crosslinking of Guar and Guar Derivatives. *SPE Annual Technical Conference and Exhibition.* 26-29 September 2004. Houston, Texas: Society of Petroleum Engineers.

LEVITT, D.B. et al., 2011. The Effect of Redox Potential and Metal Solubility on Oxidative Polymer Degradation. 14(3), pp. pp. 287-pp. 287-298

MADU, S.O. and AKINFOLARIN, A.A., 2013. *Case Histories of Drilling Challenges and Prediction of Equivalent Static Density of HPHT Wells in Niger-Delta.* Lagos, Nigeria: Society of Petroleum Engineers.

MARCUS, Y., 2012. The Cation Series. *Ions in Water and Biophysical Implications: From Chaos to Cosmos.* Dordrecht: Springer. pp. 183-187

MARESH, J.L. 2009. *Wellbore treatment fluids having improved thermal stability.* United States US7541316 B2.

MEMBER, M.W.N. and MORRIS, E.R., 1995. Solubility, solution rheology and salt-induced gelation of welan polysaccharide in organic solvents. *Carbohydrate Polymers,* 27(1), pp. 23-36

MESSLER, D. et al., 2004. *A Potassium Formate Milling Fluid Breaks the 400° Fahrenheit Barrier in a Deep Tuscaloosa Coiled Tubing Clean-out.* Lafayette, Louisiana: Society of Petroleum Engineers.

MORENO, H., 2011. Drilling Fluids Technology. *Petroskills.*

MORONI, L.P., FRASER, J.R., SOMERSET, R., JONES, A. and GUARNERI, A., 2008. Manganese-Tetraoxide-Weighted Invert Emulsions as Completion Fluids. *SPE International Symposium and Exhibition on Formation Damage Control.* 13-15 February 2008. Lafayette, Louisiana, USA: Society of Petroleum Engineers.

NORTON, I.T., SPYROPOULOS, F. and COX, P., 2010. *Practical Food Rheology - An Interpretive Approach.* John Wiley & Sons.

OSWALD, R.J., KNOX, D.A. and MONEM, M.R., 2006. *Taking Nondamaging Fluids to New Extremes: Formate-Based Drilling Fluids for High-Temperature Reservoirs in Pakistan.* Lafayette, Louisiana U.S.A.: Society of Petroleum Engineers.

RENOU, F. et al., 2013. Effect of xanthan structure on its interaction with Locust Bean Gum: towards prediction of rheological properties. *Food Hydrocolloids,* (0), RYCHLÝ, J. and MATISOVÁ-RYCHLÁ, L., Chapter 11 The Role of Oxidation in Degradation of Polymers: The Relation of Oxidation to the Light Emission from Oxidized Polymers. *Comprehensive Analytical Chemistry.* Elsevier. pp. 451-498

RAMSEY, M.S., SHIPP, J.A., LANG, B.J., BLACK, A., and CURRY, D. 1996. Cesium Formate - The Beneficial Effects of Low Viscosity and High Initial Fluid Loss on Drilling Rate - A Comparative Experiment. *SPE/IADC Asia Pacific Drilling Technology.* 9-11 September 1996. Kuala Lumpur, Malaysia: 1996 Copyright 1996, IADC/SPE Drilling Conference.

SAASEN, A. and LØKLINGHOLM, G., 2002. *The Effect of Drilling Fluid Rheological Properties on Hole Cleaning.* Dallas, Texas: Copyright 2002, IADC/SPE Drilling Conference.

SADIQ, R. et al., 2003. Evaluation of generic types of drilling fluid using a risk-based analytical hierarchy process. *Environmental Management,* 32(6), pp. 778-787

SERIGHT, R.S. and HENRICI, B.J., 1990. *Xanthan Stability at Elevated Temperatures.* SPE Reservoir Engineering, February 1990, Vol 5: No 1. Copyright 1990, Society of Petroleum Engineers pp. 52-60

SHADRAVAN, A. and AMANI, M., 2012. *HPHT 101: What Every Engineer or Geoscientist Should Know about High Pressure HighTemperature Wells.* Kuwait City, Kuwait: 2012, Society of Petroleum Engineers.

SURVASE, S.A. et al., 2007. Scleroglucan: Fermentative Production, Downstream Processing and Applications. *Food Technol. Biotechnol.,* , pp. 107-118

TEHRANI, A. 2009. *Aqueous Base Wellbore Fluids for HTHP Applications and Methods of Use.* United Kingdom EP2132277 A1.

TÓTH, K. et al., 2008. Flexibility and enzyme activity of NADH oxidase from Thermus thermophilus in the presence of monovalent cations of Hofmeister series. *Biochimica et Biophysica Acta (BBA) - Proteins and Proteomics,* 1784(5), pp. 789-795

VAN OORT, E.V., HALE, H.A., MODY, K.H. and SANJIT, R., 1996. *Transport in Shales and the Design of Improved Water-Based Shale Drilling Fluids.* 25-28 September 1996. New Orleans, USA; Society of Petroleum Engineers.

VAN OORT, E.V., BLAND, G.R., HOWARD, S.K., WIERSMA, J.R., and ROBERTSON, L., 1997. Improving HPHT Stability of Water Based Drilling Fluids. *SPE/IADC Drilling Conference.* 4-6 March 1997. Amsterdam, Netherlands: 1997 Copyright 1997, SPE/IADC Drilling Conference.

WANG, W., LU, X. and XIE, X., 2008. Evaluation of Intra-Molecular Cross-Linked Polymers. *SPE Western Regional and Pacific Section AAPG Joint Meeting.* 29 March-2 April 2008. Bakersfield, California, USA: Society of Petroleum Engineers.

WELLINGTON, S.L., 1983. Biopolymer Solution Viscosity Stabilization - Polymer Degradation and Antioxidant Use. 23(6), pp. 901-901-912

WEVER, D.A.Z., PICCHIONI, F. and BROEKHUIS, A.A., 2011. Polymers for enhanced oil recovery: A paradigm for structure–property relationship in aqueous solution. *Progress in Polymer Science,* 36(11), pp. 1558-1628

WU, Y. et al., 2012. *Development of New Polymers with Better Performance under Conditions of High Temperature and High Salinity.* Muscat, Oman: Society of Petroleum Engineers.

WYATT, N.B., GUNTHER, C.M. and LIBERATORE, M.W., 2011. Increasing viscosity in entangled polyelectrolyte solutions by the addition of salt. *Polymer,* 52(11), pp. 2437-2444

XU, L. et al., 2013. The comparison of rheological properties of aqueous welan gum and xanthan gum solutions. *Carbohydrate Polymers,* 92(1), pp. 516-522

ZHANG, Y. and CREMER, P.S., 2006. Interactions between macromolecules and ions: the Hofmeister series. *Current opinion in chemical biology,* 10(6), pp. 658-663

ZHONG, L. et al., 2013. Rheological behavior of xanthan gum solution related to shear thinning fluid delivery for subsurface remediation. *Journal of hazardous materials,* 244–245(0), pp. 160-170

Chapter 6 : APPENDIX

Clearly Different

Article for Oilfield Technology Magazine, July 2012

CLEARLY DIFFERENT

Lauren Kaminski and Siv Howard, Cabot Specialty Fluids, UK and John Downs, Formate Brine Ltd, UK, explain how cesium salts dissolved in non-aqueous solvents create a totally new class of clear heavy fluids.

Clear solids-free fluids are often required to provide well control during well construction, workover, stimulation and suspension operations in reservoir intervals. Traditionally these fluids are aqueous salt solutions ("brines"), or invert emulsions of the salt solutions in oil. The density of the clear fluids is controlled by the nature and concentration of the salts dissolved in the water phase. The absence of weighting solids in these fluids eliminates the risk of solids sag and ensures that they exert a constant/steady hydrostatic pressure over time for stable well control. The clean well environment created by the fluids eases the running, setting and activation of downhole equipment and seals. The use of clear fluids also reduces the risk of formation damage from solids invasion in the reservoir, helping to optimise oil and gas production. In order to qualify for use in those well operations where contact with hydrocarbon-bearing reservoirs is possible the clear fluid should meet the following performance criteria:

- The fluid density must be capable of controlling the highest sub-surface pressure regime.
- The fluid freezing and crystallisation temperatures should be lower than the lowest surface and subsurface temperature, corrected for pressure effects.
- The fluid must be chemically inert, or exhibit benign chemistry, under the most extreme sub-surface conditions.

- The fluid must be capable of formulation with soluble polymers, to modify rheology and/or provide fluid loss control across permeable formations.
- The fluid must be fully compatible with all of the reservoir components at reservoir temperature/pressure. It must not have any adverse effects on the permeability and strength of the reservoir rock surrounding the wellbore.
- The fluid must be fully compatible with all metallic and elastomeric well components, under the most extreme sub-surface conditions, for the duration of the operation.
- The fluid must have no potential for adverse interactions with other fluids/chemicals injected into the reservoir before or after its deployment in the well.
- The fluid must have no potential for creating hydrates in sub-surface or surface equipment, and ideally it should inhibit hydrate formation.
- The fluid must have a good HSE profile, meeting or exceeding local and international regulatory requirements – i.e. non-hazardous (toxicity, flash point, etc.) and non-polluting.
- The fluid must allow or enhance logging interpretation for accurate reservoir definition.

Figure 1. *Clear solution of cesium formate in MEG – density 2.22 g/cm³.*

Cesium formate brine

The most compliant and adaptable clear fluid currently available on the market today is cesium formate brine.[1] Over the past 12 years, water and oil-based clear fluids weighted with cesium formate have been deployed in over 300 well operations in some of the world's most demanding and challenging gas field developments. The advent of cesium formate brine in 1999 enabled the oil industry to begin enjoying the full economic benefits of creating low-skin openhole completions in deep high angle HPHT gas wells. Reviews published in 2010[2] and 2011[3] found that drilling and completing deep HPHT gas reservoirs with heavy cesium formate brines enhanced project economics by:

- Virtually eliminating well control and differential pipe sticking incidents.
- Enabling the drilling of long high angle wells within narrow drilling windows.
- Typically reducing offshore HPHT well completion times by 30 days or more.
- Promoting sustained high rate gas production, in several cases delivering 90% of the recoverable gas reserves within seven years from start-up.
- Improving the definition and visualisation of the gas reservoirs.
- Eliminating the need for clean-ups, stimulation treatments or any other form of intervention to remove formation damage caused by the drilling fluid.

Clear invert emulsions

Clear invert oil emulsion (CIOE) fluids weighted with cesium formate brine have been used in the field since 2001 as completion fluids in oil reservoirs.[4] The use of solids-free cesium-weighted CIOE fluids in completion operations reduces the risk of formation damage from solids invasion and adverse interactions with oil-based mud filtrates. The only drawback with CIOE fluids is that the brine: oil ratio restrictions for stable invert emulsions means that their density ceiling is 1.52 g/cm³ with cesium formate brine as the internal phase. This density limitation on invert oil emulsions led to the investigation of whether there were other ways of creating heavy non-aqueous fluids weighted with cesium salts.

Non-aqueous solvents

The first task was to make a shortlist of benign and environmentally acceptable non-aqueous fluids already in use by

Table 1. Some non-aqueous solvents and their properties

Solvent	Density (g/cm3) at 20 °C	Boiling point (°C)	Freezing point (°C)	Flash point* (°C)	Viscosity at 20 °C (cP)	Thermal conductivity (W/m/°C)
Monoethylene Glycol (MEG)	1.115	197	-13	126	16.9	0.26
Diethylene Glycol (DEG)	1.118	245	-9	154	35.7	0.19
Triethylene Glycol (TEG)	1.125	288	-4	177	49.0	0.19
Butyl Glycol (EGMBE)	0.90	171	-77	65	2.9	0.17
Glycerol	1.26	290	17.8	177	1499	0.28
Mineral oil	0.805	225	-29**	102	2.4	0.16

*Closed cup measurement. **Pour Point.

the oil industry (and approved by regulatory authorities) that might potentially serve as solvents for cesium salts. The short list of five solvents selected for testing comprised three common ethylene glycols, a glycol ether and glycerol. The properties of these fluids are compared in Table 1 with those of a mineral oil commonly used as the continuous fluid phase of oil-based muds.

All of the solvents selected are fully miscible with water in all proportions, but only the butyl glycol is miscible with oil. The butyl glycol (otherwise known as ethylene glycol monobutyl ether or EGMBE) is closest in its physical properties to those of mineral oil used in drilling fluids, particularly in terms of viscosity and thermal conductivity. The solvents all score highly in environmental rankings, rating Gold or Category E in the PARCOM Offshore Chemical Notification System. In fact MEG and glycerol are rated PLONOR – i.e. they feature in the OSPAR list of substances used and discharged offshore, which are considered to pose little or no risk to the environment.

The ethylene glycols are mainly used in gas dehydration and gas hydrate inhibition, exploiting their low water activity (0.034 A_w @25 °C). The EGMBE also has a low water activity (0.045 A_w @25 °C) but is primarily used as a mutual solvent in well stimulation operations. Glycerol (0.122 A_w @25 °C) is listed as being used a gas hydrate inhibitor.

Cesium salt solvency tests

The individual solubilities of high purity dry cesium formate, cesium acetate and cesium phosphate powders were determined for each of the solvents. Increasing amounts of the salts were added to each solvent over a number of days until the solutions were fully saturated at room temperature (around 20 °C). Tables 2 to 4 summarise the outcome of the tests, showing the percentage w/w salt solubility achieved for each salt-solvent combination compared with salt in water. The tables also show the density and water activity of the saturated solutions. Solution densities were measured using a Mettler Toledo DM-40 Densitometer. Water activity was measured with a Rotronic water activity meter.

The results show that MEG is a very good solvent for all three cesium salts. Cesium formate was found to be soluble to 82.9% w/w in MEG, yielding a clear solution with a density of 2.22 g/cm^3 (Figure 1). Cesium phosphate was the next most soluble salt at 68.4% w/w, giving a solution density of 2.01 g/cm^3. Cesium acetate was the least soluble of the three cesium salts in MEG, but a solution concentration of 61.1% w/w and density of 1.67 g/cm^3 was still achieved.

The general trend in the higher ethylene glycols (DEG and TEG) was for the solvency, and the resulting solution density, to decrease with increasing molecular weight of the glycol. So the cesium salts solubilised in DEG to yield to solution densities in the medium 1.51-1.67 g/cm^3 range, but only gave densities of around 1.39 g/cm^3 in TEG. Dissolving dry cesium formate in a polyethylene glycol of molecular weight 200 at 20 °C gave a solution density of 1.37 g/cm^3 with a water activity of 0.055. The only exception to this general trend was the relatively high solubility of cesium acetate in TEG, giving a solution density of 1.75 g/cm^3. In fact cesium acetate powder exhibited good solubility in all of the non-aqueous solvents, always giving solution densities of > 1.5 g/cm^3.

The glycol ether (EGMBE) was not a good solvent for cesium formate or cesium phosphate but, surprisingly; it did dissolve cesium acetate to a final solution concentration of 65.4% w/w. The density of the saturated cesium acetate solution in EGMBE was a respectable 1.52 g/cm^3. The original density of the base solvent was just 0.90 g/cm^3.

Glycerol was found to be a moderately good solvent for all of the cesium salts. The best performer was a 63.8% w/w cesium formate in glycerol solution with a density of 1.96 g/cm^3.

Some preliminary solubility test results were also obtained with methanol as a solvent. This lower alcohol does not fit the profile of a benign non-aqueous solvent, being quite hazardous and toxic, but it is used in the field in gas dehydration and hydrate inhibition operations. Cesium formate and cesium acetate were found to be highly soluble in methanol, yielding saturated solution of density 1.52 g/cm^3 and 1.57 g/cm^3 respectively. These solution densities represent a significant increase on the base solvent density of 0.796 g/cm^3.

Curiously, the solubility of cesium formate in MEG decreased with increasing temperature over the range 10 – 40 °C. At the time of writing, no further work had been done to see if a) the decrease continued at higher temperatures and b) the same phenomenon occurred with other salt/solvent combinations.

In general, the water activity of the non-aqueous solvents increased when saturated with the cesium salts. The increase in water activity was greatest with cesium phosphate in solution, and the least with cesium formate. The exceptions to this rule were:

- The water activity of glycerol dropped slightly when saturated with cesium formate or cesium acetate.
- The water activity of EGMBE dropped slightly when saturated with cesium formate.

Conclusions

It has been found that three cesium salts are moderately to highly soluble (i.e. 16 - 83% w/w) in a range of benign non-aqueous solvents currently used by the oil and gas industry in gas dehydration, hydrate inhibition and hydraulic control applications. In the best case, the solubilisation of cesium formate powder in MEG produced a clear non-aqueous fluid with a density of 2.22 g/cm^3 at 20 °C. This is a significant improvement on the fluid densities achievable with clear invert oil emulsions weighted with cesium formate brine.

These novel solids-free high-density water-free fluids could potentially be used in drilling, completion, workover and packer or suspension operations to provide well control. At the very least they could be used as weighted pills for placement in wells to (e.g.) melt hydrate plugs or prevent hydrates from forming. However, further characterisation and qualification work will need to be done on the fluids before they can be applied in the field. This further work might include investigations into:

- Formulation of mixed potassium/cesium salts in the solvents. Potassium formate and potassium acetate are known to be soluble to 40% w/w in MEG, and they improve the gas dehydration efficiency of MEG, DEG and TEG[5].
- Solubility of sodium and rubidium salts in non-aqueous solvents. It is already known that sodium formate is moderately soluble in MEG.[6]
- Measurement of the thermal conductivity of the solutions. It is possible that some of these novel heavy fluids will have very low thermal conductivities and good thermal insulation properties.

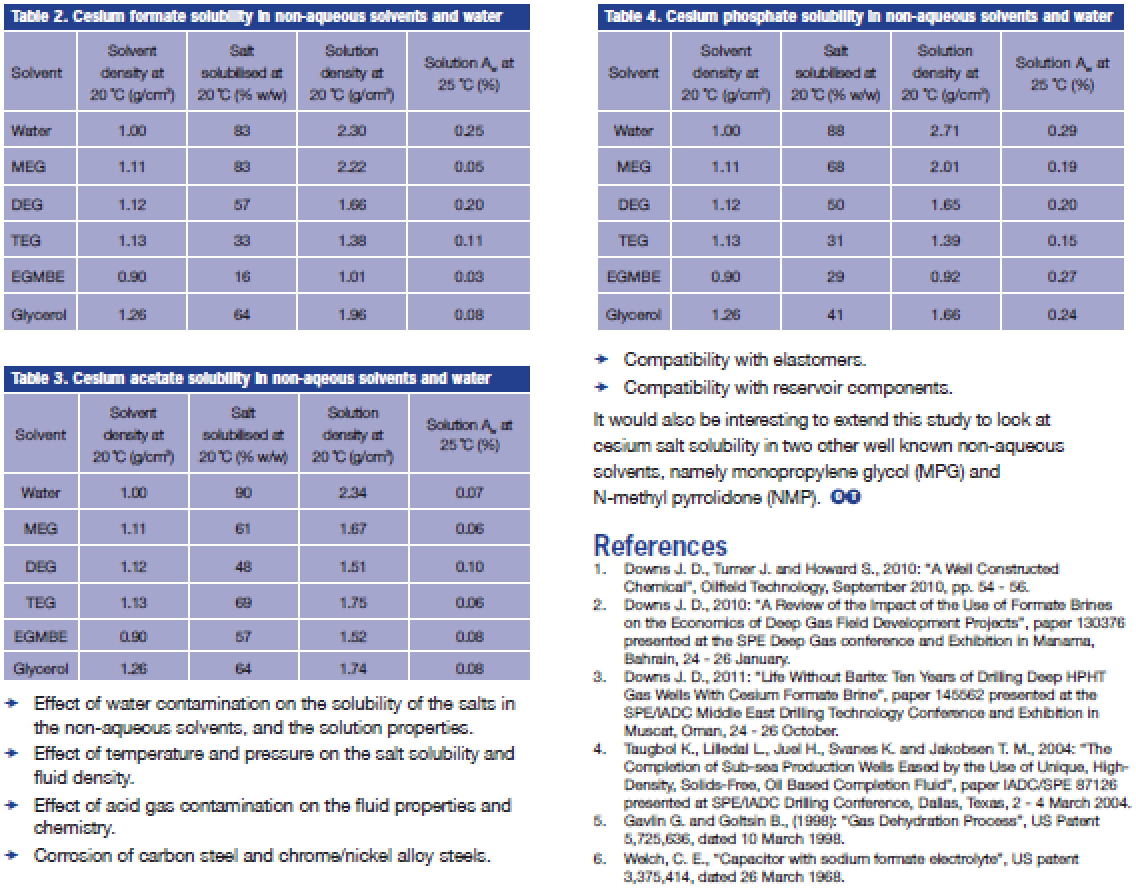


Table 2. Cesium formate solubility in non-aqueous solvents and water

Solvent	Solvent density at 20 °C (g/cm³)	Salt solubilised at 20 °C (% w/w)	Solution density at 20 °C (g/cm³)	Solution A_w at 25 °C (%)
Water	1.00	83	2.30	0.25
MEG	1.11	83	2.22	0.05
DEG	1.12	57	1.66	0.20
TEG	1.13	33	1.38	0.11
EGMBE	0.90	16	1.01	0.03
Glycerol	1.26	64	1.96	0.08

Table 3. Cesium acetate solubility in non-aqeous solvents and water

Solvent	Solvent density at 20 °C (g/cm³)	Salt solubilised at 20 °C (% w/w)	Solution density at 20 °C (g/cm³)	Solution A_w at 25 °C (%)
Water	1.00	90	2.34	0.07
MEG	1.11	61	1.67	0.06
DEG	1.12	48	1.51	0.10
TEG	1.13	69	1.75	0.06
EGMBE	0.90	57	1.52	0.08
Glycerol	1.26	64	1.74	0.08

- Effect of water contamination on the solubility of the salts in the non-aqueous solvents, and the solution properties.
- Effect of temperature and pressure on the salt solubility and fluid density.
- Effect of acid gas contamination on the fluid properties and chemistry.
- Corrosion of carbon steel and chrome/nickel alloy steels.

Table 4. Cesium phosphate solubility in non-aqueous solvents and water

Solvent	Solvent density at 20 °C (g/cm³)	Salt solubilised at 20 °C (% w/w)	Solution density at 20 °C (g/cm³)	Solution A_w at 25 °C (%)
Water	1.00	88	2.71	0.29
MEG	1.11	68	2.01	0.19
DEG	1.12	50	1.65	0.20
TEG	1.13	31	1.39	0.15
EGMBE	0.90	29	0.92	0.27
Glycerol	1.26	41	1.66	0.24

- Compatibility with elastomers.
- Compatibility with reservoir components.

It would also be interesting to extend this study to look at cesium salt solubility in two other well known non-aqueous solvents, namely monopropylene glycol (MPG) and N-methyl pyrrolidone (NMP).

References

1. Downs J. D., Turner J. and Howard S., 2010: "A Well Constructed Chemical", Oilfield Technology, September 2010, pp. 54 - 56.
2. Downs J. D., 2010: "A Review of the Impact of the Use of Formate Brines on the Economics of Deep Gas Field Development Projects", paper 130376 presented at the SPE Deep Gas conference and Exhibition in Manama, Bahrain, 24 - 26 January.
3. Downs J. D., 2011: "Life Without Barite: Ten Years of Drilling Deep HPHT Gas Wells With Cesium Formate Brine", paper 145562 presented at the SPE/IADC Middle East Drilling Technology Conference and Exhibition in Muscat, Oman, 24 - 26 October.
4. Taugbol K., Lilledal L., Juel H., Svanes K. and Jakobsen T. M., 2004: "The Completion of Sub-sea Production Wells Eased by the Use of Unique, High-Density, Solids-Free, Oil Based Completion Fluid", paper IADC/SPE 87126 presented at SPE/IADC Drilling Conference, Dallas, Texas, 2 - 4 March 2004.
5. Gavlin G. and Goltsin B., (1998): "Gas Dehydration Process", US Patent 5,725,636, dated 10 March 1998.
6. Welch, C. E., "Capacitor with sodium formate electrolyte", US patent 3,375,414, dated 26 March 1968.

Clearly Cloudy

Poster Presentation for SPE Bergen, April 2013

CLEARLY CLOUDY – FINDING A CLOUDING GLYCOL SYSTEM FOR FORMATE BRINES

L. Kaminski, Cabot Specialty Fluids; **J.D. Downs,** Formate Brine Ltd.; **S.K. Howard,** Cabot Specialty Fluids

Towards the perfect shale drilling fluid

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

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

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

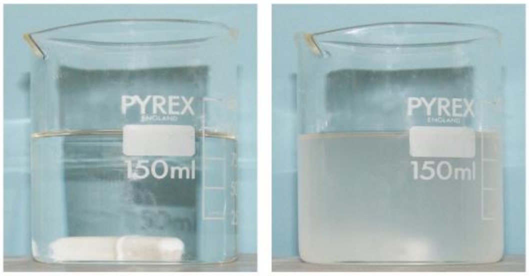


Figure 1 1.85 g/cm³ cesium formate with 5% PEG 400 at room temperature (left) and heated to 60°C (right)

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

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

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

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

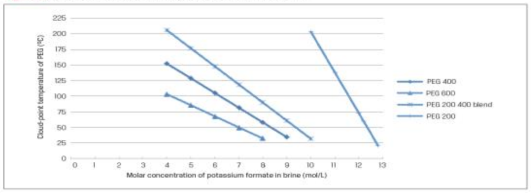
Experimental

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

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

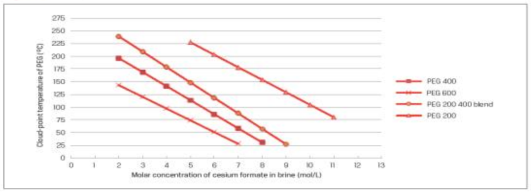
Property	PEG 200	PEG 400	PEG 600
Viscosity @ 100°C (CSt)	4.3	7.3	10.8
Flash point, closed cup (°C)	185	227	185
Solubility at 5% in water @ 25°C	Complete	Complete	Complete
Freezing point (°C)	-65	4 – 8	15 – 25
Density (g/cm³ @ 20°C)	1.124	1.125	1.126
Toxicity – human hazard	Non-hazardous	Non-hazardous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

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



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

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

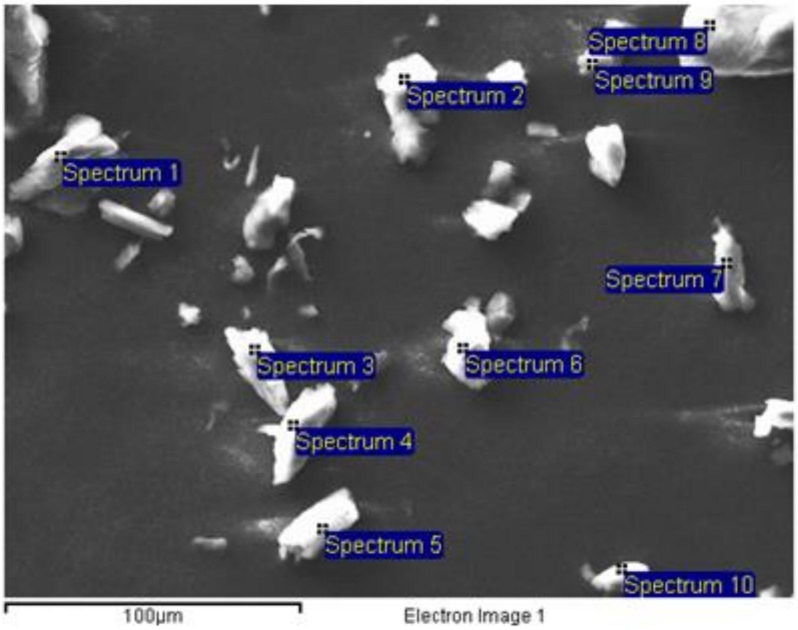


This preliminary work demonstrates that benign low-molecular-weight polyethylene glycols are effective clouding agents in high-density single-salt potassium and cesium formate brines. Further study is required to check PEG behaviour in mixed potassium/cesium formate brine blends with common drilling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

The 20th SPE Bergen One Day Seminar
April 10th 2013 | Bergen, Norway

X-Ray Elemental Analysis (SEMEDAX) on Xanvis®

Sample: Xan-vis
Type: Default
ID:

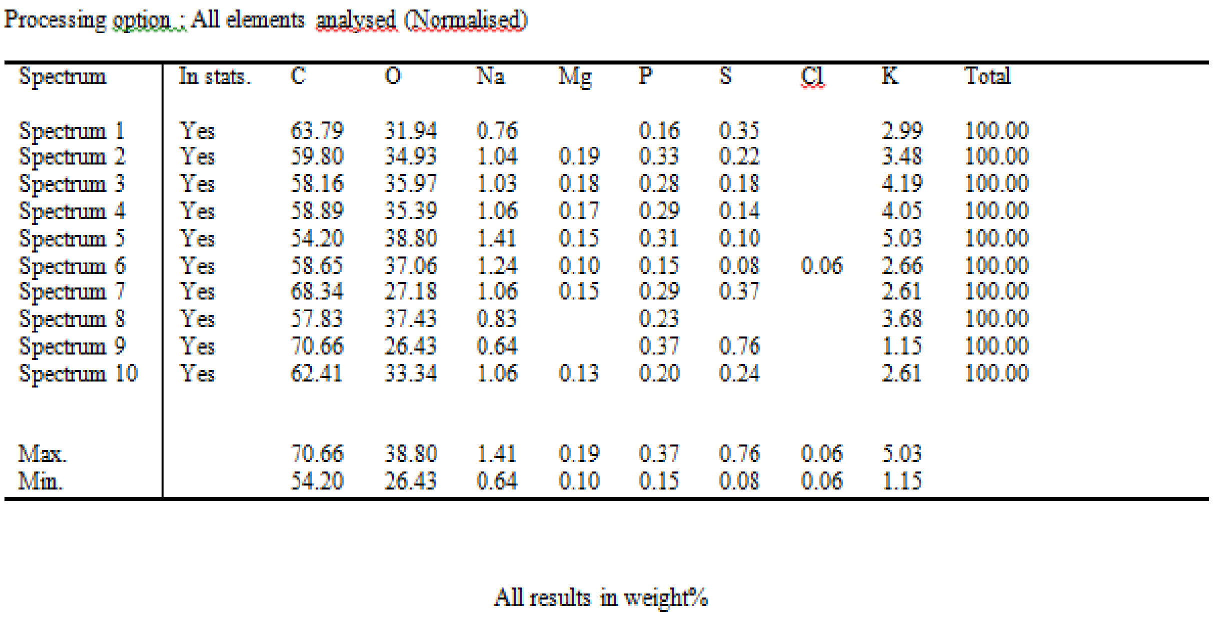


Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 4

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	62.41	70.10
O K	33.34	28.11
Na K	1.06	0.62
Mg K	0.13	0.07
P K	0.20	0.09
S K	0.24	0.10
K K	2.61	0.90
Totals	100.00	



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Na	Mg	P	S	Cl	K	Total
Spectrum 1	Yes	63.79	31.94	0.76		0.16	0.35		2.99	100.00
Spectrum 2	Yes	59.80	34.93	1.04	0.19	0.33	0.22		3.48	100.00
Spectrum 3	Yes	58.16	35.97	1.03	0.18	0.28	0.18		4.19	100.00
Spectrum 4	Yes	58.89	35.39	1.06	0.17	0.29	0.14		4.05	100.00
Spectrum 5	Yes	54.20	38.80	1.41	0.15	0.31	0.10		5.03	100.00
Spectrum 6	Yes	58.65	37.06	1.24	0.10	0.15	0.08	0.06	2.66	100.00
Spectrum 7	Yes	68.34	27.18	1.06	0.15	0.29	0.37		2.61	100.00
Spectrum 8	Yes	57.83	37.43	0.83		0.23			3.68	100.00
Spectrum 9	Yes	70.66	26.43	0.64		0.37	0.76		1.15	100.00
Spectrum 10	Yes	62.41	33.34	1.06	0.13	0.20	0.24		2.61	100.00
Max.		70.66	38.80	1.41	0.19	0.37	0.76	0.06	5.03	
Min.		54.20	26.43	0.64	0.10	0.15	0.08	0.06	1.15	

All results in weight%