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Engineering

**Master's Thesis:  
Innovative completion fluids**

Student: Leyla Aliyeva S263255

Supervisor: Prof. Ing. Raffaele Romagnoli

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## **Abstract**

According to the current technologies during the last decade more attention has been given to design and develop novel completion fluids and additives which can meet most of requirements and challenges in comparison with conventional types of fluids. The aim of this work is to summarize and perform an extensive overview for different types of completion brines including the additives, to make a comparison and underline their main benefits and drawbacks. It describes development of innovative completion fluids which are cost effective and less problematic.

## **1. Introduction**

Completion fluids are the solids-free liquids which are used to perform downhole operations after gas and oil wells have been drilled. They help to prepare, clean-out, repair and complete the wellbore. Completion brines induce the pressure on the well walls to achieve mechanical control (to keep a stable wellbore), so that to escape the collapse, particularly because the liquid is made of non-damaging plugging material. Consequently, an impermeable filter cake may form. Chemical composition of fluids must be consistent with reservoir and formation fluids. Well known completion fluids are brines such as mixtures of water with bromides, formates, chlorides.

Other roles of completion fluids are to maintain pressures of formation, to take away from the well the solids, to transfer to a given point downhole the treating fluids.

The wrong selected completion fluid may damage the formation and cause the reduction of rock permeability by their invasion.

### **1.1 The main functions of completion fluids:**

- 1) Cleanout of wellbore
- 2) Well control
- 3) Corrosion prevention
- 4) Formation pressure control by means of density
- 5) Skin damage minimization
- 6) Treating chemicals removal

- 7) Solids' transport and circulation
- 8) Preserve production zones from damage

Completion fluids must preserve production zones from damage and ensure stability at downhole and surface conditions. They must be environment friendly, safely handled and with exposure control. From economical point of view brines also must be cost-effective.

Clear brines are prepared from salts dissolved in a given volume of water. They do not include any solids and must be stable. They can be designed from a single salt or a mixture of more than two salts dissolved and they must be compatible with each other.

The requirements for clear brines to be able to perform with high efficiency:

- To be solids-free
- To hinder the shale
- Ability to be reused
- To have different densities range

## **1.2 Selection of Completion Fluids**

There are different types of brines used as completion fluids. By altering the salts concentrations in solution densities of brines can be adjusted. Calculation of brine mixture composition is not straightforward as these salts are soluble in water. The preparation of brines is made with the use of empirical blend charts. These charts are given by suppliers and manufacturers. All brines are formed from known basic materials which include dry salts as KCl and CaCl<sub>2</sub> and stock brines as CaBr<sub>2</sub> 14.2 lb/gal.

Density and crystallization temperature requirements are significantly affecting the manner in which these materials are mixed. Environmental conditions must be matched with crystallization temperature. According to the API standard procedures crystallization temperature and density are defined.

Brines used as completion fluids in highly permeable zones may require addition of bridging solids in order to control fluids losses which are induced due to formation damage. When the producing zone includes unconsolidated sands brines may also be hard to use as they do not prevent washouts and slumping.

Deposition of a filter cake on the walls of the hole can prevent slumping to occur, so as the pressure overbalance is applied on the formation face. Some clear brines are characterized by higher viscosity or viscous pills use can be requires to be used when millings, cuttings, etc. must be removed out of the hole, as they have no yield point, low viscosities and carrying capacity.

### **1.3 Completion Fluid Types**

There are different types of completion fluids. They are divided depending on the application.

- 1) Clear, solids-free brines
- 2) Polymer-viscosified brines
- 3) Oil-based, water-based or converted muds

Water-based fluids – this type is related to drilling muds which have been modified in order to use as completion fluids. They contain solids, therefore this type must be avoided to be exploited during completion, unless the well is perforated in under-balanced condition and set on flowing production. The mud solids may damage the formation. For instance, barite is a known mud additive which can damage the formation and is hard to remove it chemically.

Oil-based fluids -they are used to preserve water-sensitive clay from chemical damage. This type contains both suspended and dissolved fluids of different amounts. These solids can form precipitates, plug formation pores and settle over time. However, these fluids are more expensive in comparison with water-based muds and less damaging.

Clear Brine fluids – the most widespread are clear brines. Nowadays the most of completion fluids are solid-free or with minimum solids amount. Inorganic salts are

used to prepare clear brines in order to achieve higher density liquid for more hostile environment. Clear brines can incorporate one type of dissolved salt or a blend of more than 2 compounds which must be compatible with each other. They control reservoir pressures being solid-free clear brines, which can minimize formation damages. Brines with higher density need especial handling. The densities range is from 8.5 – 19.2 lb/gal. Disadvantages are fluid crystallization and excessive corrosion.

#### **1.4 Parameters of completion fluids:**

Completion fluids are characterized by properties such as turbidity (clarity), density, specific gravity, pH values, viscosity, gel strength and holding capacity.

##### **1) Turbidity (Clarity) and Density**

Turbidity (clarity) and density are the main properties characterizing clear brines.

Turbidity is an indicator of a degree to which due to the presence of suspended particles the liquid loses its transparency. The turbidity depends on the purity of liquids. The unit of measurement is Nephelometer Turbidity Units (NTUs). The turbidity is measured by means of nephelometer or turbidimeter.

Nephelometry is a method of measuring the amount of light which is scattered at a certain angle after beaming the light on a sample. The industry standard measurement is lower than 30 NTUs per sample.

NTU value will be large if the fluid contains undissolved salts, drill solids, etc., because the turbidity will be high. Consequently, by cleaning the fluid the value of NTU will decrease. Therefore, in completion operations low values of NTU are preferred.

Density of completion fluids is high for safety reasons. They can be overbalanced or heavy enough in order to flow inside the formation and stop the blowout possibility.

In the table below different clear brine types and density ranges are shown:

<b>Brine type</b>	<b>Density range (lb/gal)</b>	<b>Typical Density (lb/gal)</b>
NaCl	8.33 – 10.0	8.4 – 10.0
KCl	8.33 – 9.7	8.4 – 9.0
NH <sub>4</sub> Cl	8.33 – 8.9	8.4 – 8.7
NaBr	8.33 – 12.7	10.0 – 12.5
NaCl / NaBr	8.33 – 12.5	10.0 – 12.5
NaHCO <sub>2</sub>	8.33 – 11.1	9.0 – 10.5
KHCO <sub>2</sub>	8.33 – 13.3	10.8 – 13.1
NaHCO <sub>2</sub> / KHCO <sub>2</sub>	8.33 – 13.1	8.4 – 12.7
KHCO <sub>2</sub> / CsHCO <sub>2</sub>	8.33 – 20.0	13.1 – 18.3
CaCl <sub>2</sub>	8.33 – 11.8	+/- 9.0 – 11.6
CaBr <sub>2</sub>	8.33 – 15.3	+/- 12.0 – 14.2
CaCl <sub>2</sub> / CaBr <sub>2</sub>	8.33 – 15.1	11.7 – 15.1
ZnBr <sub>2</sub>	+/- 12 – 21.0	19.2 – 21.0
ZnBr <sub>2</sub> / CaBr <sub>2</sub>	+/- 12 – 19.2	+/- 14.0 – 19.2
ZnBr <sub>2</sub> / CaBr <sub>2</sub> / CaCl <sub>2</sub>	+/- 12 – 19.1	+/- 14.2 – 19.2
CsHCO <sub>2</sub>	+/- 8.33 – 20.0	13.2 – 19.2

Table 1. Conventional clear brines

By dissolving salts in water density can be obtained, because density will be proportional to the amount of salt dissolved in water. Salts are characterized by high solubility in water. The densities which can be obtained may reach up to 21 lb/gal. The salt-water ratio is becoming smaller when the solubility increases. In some cases, clear brines may have more salt than water included in their composition.

The salts maximum solubility in water is shown in the table below:

<b>Salt</b>	<b>Sol wt %</b>	<b>Density lb/gal</b>	<b>Specific Gravity</b>	<b>Lb Salt</b>	<b>Lb Water</b>
NaCl	26	10.0	1.200	109	311
KCl	24	9.7	1.164	98	309
NaBr	46	12.7	1.525	245	288
CaCl <sub>2</sub>	40	11.8	1.416	198	298
CaBr <sub>2</sub>	57	15.3	1.837	366	194
ZnBr <sub>2</sub>	78	21.0	2.521	688	194
NaHCO <sub>2</sub>	50	11.1	1.329	231	235
KHCO <sub>2</sub>	78	13.3	1.595	434	125
CsHCO <sub>2</sub>	84	19.17	2.30	676.3	128.8

Table 2. Maximum solubility of salts

## 2) pH values

Formation water is characterized by pH from 4 to 9, whereas pH range of completion fluids is between 8 and 12. When alkaline fluid enters the rock of the reservoir, the siliceous minerals and clay textures are becoming affected by clay minerals and cement dissolution and also pore plugging may appear due to the detachment of particles. The pugging of pores depends on the dimensions of particles. So, critical pH value, above which the detachment occurs, must be obtained. For this purpose, alkaline sensitivity analysis is applied. In order to avoid or minimize formation damage completion fluids must be designed at pH values which are lower than the pH critical value.

## 3) Wellbore temperature

Volume of brine changes as the temperature changes. Therefore, temperature is a parameter that must be taken into account. Density also will decrease due to the thermal expansion, as the temperature increases. So, if the brine cannot control the formation pressure the well stability may suffer. Temperature also affects corrosion rate and additives.

Examples of CaCl<sub>2</sub> brine density reduction because of the thermal expansion are represented on the next graph.

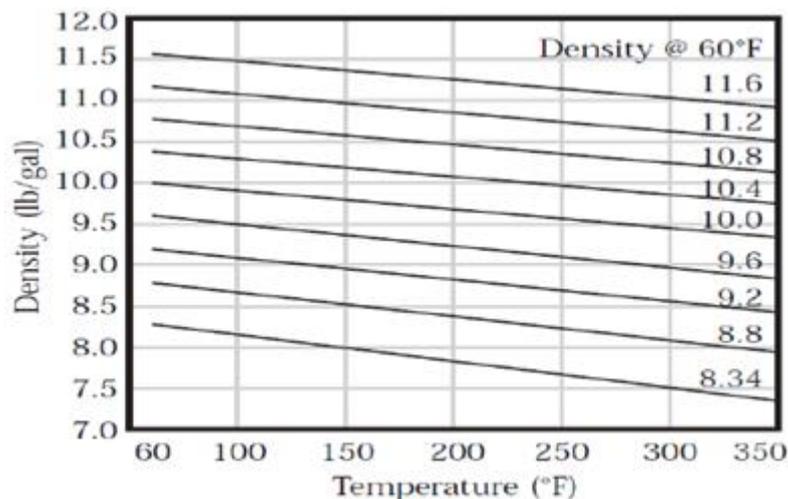


Figure 1. CaCl<sub>2</sub> density reduction in case of thermal expansion.

#### 4) Crystallization temperature

Each brine is characterized by crystallization/freezing temperature going below which the brine will freeze. As the brine composition includes dissolved salts in water, the crystallizing temperature will be led to lower till the eutectic point. The lowest temperature at which the liquid is present in the system is called eutectic temperature.

On the next figure there is shown the density effect on the crystallization temperature of CaCl<sub>2</sub> brine.

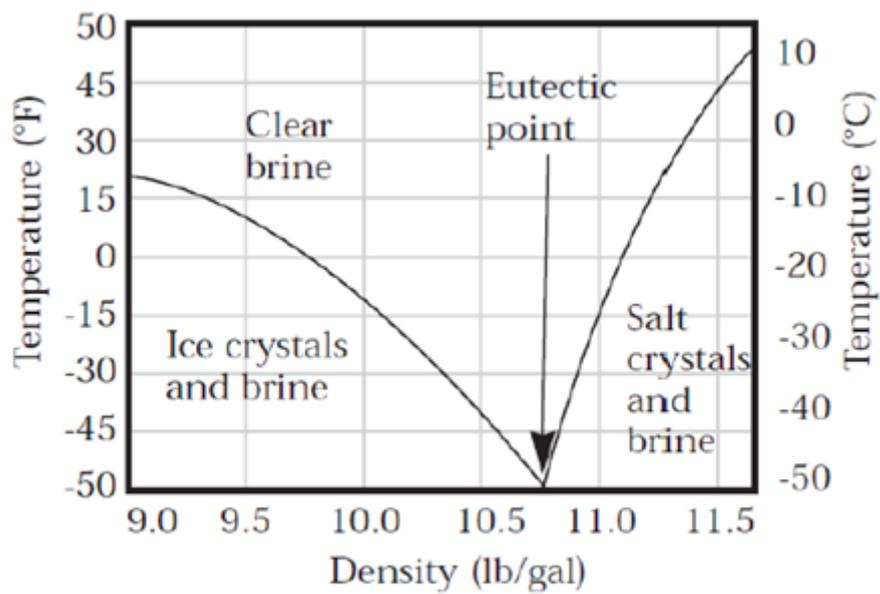


Figure 2. Density effect of CaCl<sub>2</sub> brine on the crystallization temperature.

When freezing occurs there is possibility to measure three crystallization points.

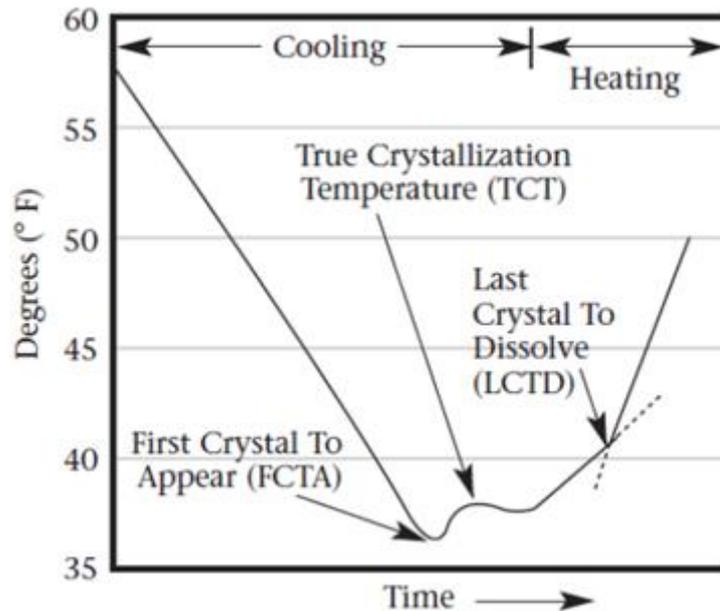


Figure 3. Different points of crystallization

First Crystal To Appear (FCTA) – as the temperature decreases the first visible salt crystal appears. This point is the lowest point on the Crystallization curve. It includes the cooling which is under TCT (True Crystallization Temperature) known as the super-cooling effect.

True Crystallization Temperature (TCT) – at this temperature the brine solution becomes fully saturated relatively to the least soluble salt. TCT is represented on the curve as a temperature increase after the super-cooling minimum.

Last Crystal to Dissolve (LCTD) – it is temperature at which the last crystal of salt disappears as the temperature continues to increase. The contamination percentage of solution affects LCTD.

Concentration of salt dissolved in brine solution depends on the temperature. Because offshore environments are characterized by cold climates, the temperature must be taken into account. Salt will precipitate from the solution under a given temperature. The crystallization temperature of brine will cause the crystals of salt to form as the pressure grows.



Figure 4. Precipitated salt crystals

Hot climates also affect the brine solution. As the brine is heated more salts may be dissolved (extra salts). As it was mentioned before, True Crystallization Temperature (TCT) is temperature at which each individual salt will saturate the water. So, TCT is extremely Important parameter which must be considered in Completion operations.

Normally, brines with lower TCT values are used (lower than actual environment temperature). The standard minimum TCT range required is from  $-9^{\circ}\text{C}$  to  $-7^{\circ}\text{C}$  ( $15^{\circ}$  to  $20^{\circ}\text{F}$ ). Brine volume does not increase during freezing because salt (solid) crystals have a smaller specific volume than brine volume. Therefore, pumps and fluid lines are not affected.

In the next figures there are shown different crystallization temperatures for different brines.

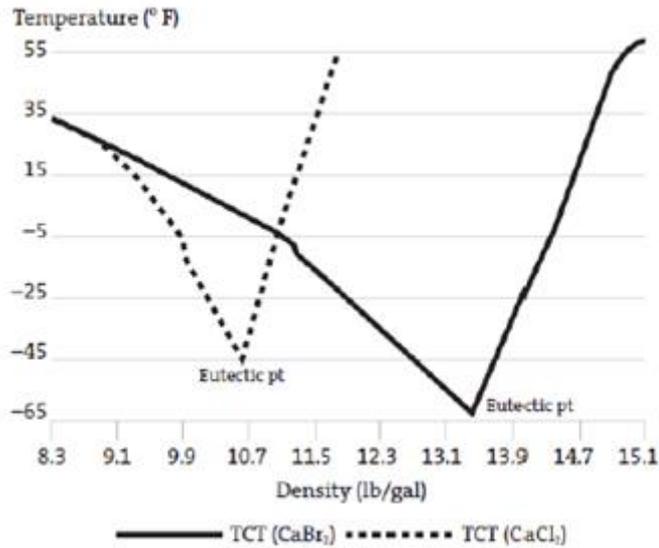


Figure 5. Crystallization temperature curves for CaBr<sub>2</sub> and CaCl<sub>2</sub>

As we can see from figure 5, eutectic temperature for CaBr<sub>2</sub> is higher than that for CaCl<sub>2</sub>.

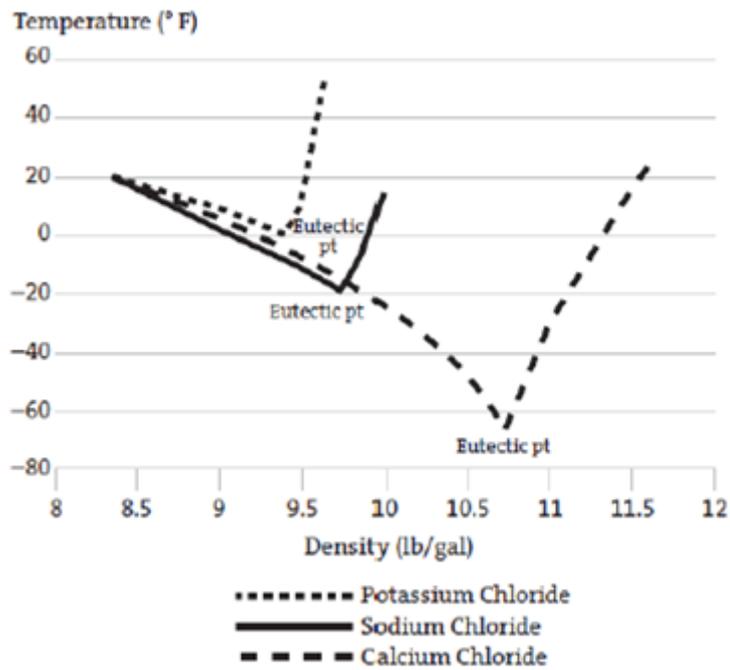


Figure 6. Crystallization temperature curves for KCl, NaCl, CaCl<sub>2</sub>

As it can be observed, each brine has its own eutectic temperatures.

## **5) Chemical compatibility**

Brine composition must be chemically compatible with the formation and its fluids. Because of incompatibility between formation water, hydrocarbons and brine system formation damage may happen.

An issue of chemical incompatibility may lead to migration and swelling of the formation clay which can cause the reservoir pores block. Therefore, to be compatible the brine system must have approximately the same amount of dissolved salt as in the formation fluid.

Another problem may be induced by inorganic materials deposits which lead to the chemical reaction between the formation fluids and the brine system, and therefore as a consequence to porosity reduction. Generation of emulsions causes the plugging of pores.

Detailed analysis of formation fluids in the laboratory helps to create a compatible brine system which will save the rig time and final cost.

## **6) Corrosion monitoring**

Formation gases, such as CO<sub>2</sub>, H<sub>2</sub>S, and oxygen introduced by means of contaminated fluids are important, because they play a role in the metal corrosion. Brines and water-base drilling muds also affect all kinds of metal casing strings and drilling equipment and causing corrosive effect. Corrosion deteriorates all metal made equipment such as pipes, tools, casing, containers, also can appear in the surface equipment (pumps, lines, pits, pipes, etc.) and in the bottom hole equipment.

## **7) Environmental impact**

Brines and salts may harm health, for example some of them are hygroscopic (absorbing water from different sources), so the skin may burn if brine will be in contact with it. Another example is a dry calcium salt which in contact with water releases heat (extremely exothermic). The temperature range is 180-200°F. Personal Protective Equipment (PPE) such as rubber boots, gloves, slicker suits, goggles and

a face shield must be provided. Eyes and skin must be immediately washed with water.

### 8) Economical point of view

Virtual Completion Solutions (VCS) is a computer program used to design and simulating multiple scenarios and operations, establishing flow regimes, pump rates, displacements, and chemical clean-up efficiency. So, it is used to plan brine systems with the minimal damaging impact for the well.

### 9) Damage types

There are two kind of damage mechanisms referred to the completion type: Completion and Formation damages.

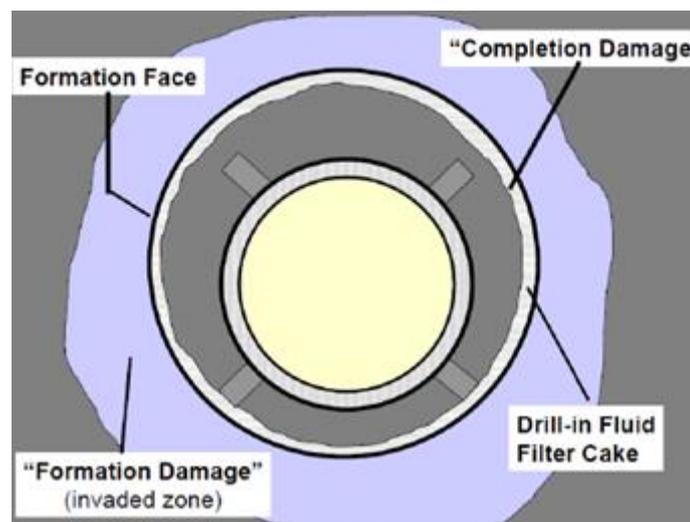


Figure 7. Well damage types

Completion damage – such materials as contaminants, residue or junk may cause damage of the reservoir formation due to invasion into the open-hole.

Improper selection of the completion fluid may lead to one of the greatest completion damages – shale inhibition. The fluid becomes contaminated by reactive clays, so the chemical treatment is needed which is aggressive and will damage reservoir formation.

Another completion damage may happen due to the left behind residue due to drilling operation. It will cause pores plugging if clean-up phase was not made properly.

Formation damage – it is related to the damage of the permeability.

Fluid invasion causes damage, so to inhibit intrusion it is important to choose completion fluid with similar chemistry as formation fluid has.

## 2. Clear Brine systems

### 2.1 Clear Brines

Brines are water-based mixture of inorganic salts used like well-control fluid during completion operations. These fluids are solids-free and does not include any particles which can damage or plug a producing formation. The salts contained in brines prevent undesirable reactions of formation like clay swelling. Brines are prepared with the use of different salts achieving density ranges from 8.4 ppg up to 20 ppg. Simple brine systems comprise calcium chloride, sodium chloride and potassium chloride. Zinc, iodine or bromide salts are contained in more complex brines. These types of brines are costly and corrosive.

#### 2.1.1 Clear Brine Fluids – Halides

TETRA calcium halide brines are exploited as completion fluids. These brines reduce possibility of formation damage induced by shale dispersion and solid invasion. They are divided into single salt and multi-salt blends.

Single salt brines are prepared from one salt. Their density range varies from value slightly above of water density (as 3% potassium chloride) up to 11.6 lb/gal calcium chloride or 15.1 lb/gal calcium bromide.

Multi-salt brines are applied in order to get fluids at a lower cost to higher densities. The most widely used two-salt blends are sodium chloride/bromide and calcium/chloride bromide and three-salt brines are zinc bromide/calcium bromide/calcium chloride. These blends are applied at the temperatures 30°F and 60°F.

Clear Brines are divided in 2 categories:

- Monovalent Brines

Sodium Chloride NaCl – this salt is used to prepare completion brine with density range from 8.4 lb/gal to 10 lb/gal. If NaCl is liquid it has temperature (TCT) of 23°F (-5°C) and density of 10 lb/gal. But if liquid NaCl is out of reach, then dry salt NaCl can be added to the drill water. Such brine type is used to reduce the water activity

(Aw) and therefore to prevent shale inhibition. It has high density, reduced gas hydrate formation potential and low crystallization point. NaCl brine is characterized by pH range from 6.5 to 7.0 and clarity lower than 3 NTU. A maximum density up to 12.5 lb/gal can be achieved by means of adding NaBr brine to NaCl mixture.

This type is used for shallow wells characterized by low pressures. It also can be used to change and regulate other brines densities. It is often chosen because of its low cost and wide availability.

To make 1 bbl (42 gal) of Sodium Chloride Brine (based on the using 100% NaCl):

<b>Density at 70°F (lb/gal)</b>	<b>NaCl (%)</b>	<b>H2O (bbl)</b>	<b>NaCl (lb)</b>	<b>Freezing Point (°F)</b>
8.4	1.0	0.995	3.5	+31
8.6	4.5	0.985	16.4	27
8.8	7.5	0.973	27.8	24
9.0	10.8	0.960	40.7	19
9.2	13.9	0.947	53.7	14
9.4	17.0	0.933	67.2	9
9.6	20.0	0.918	80.7	3
9.8	23.0	0.902	94.8	-5
10.0	26.0	0.888	109.0	30 TCT

Table 3. Components used to make Sodium Chloride brine

Sodium Bromide NaBr – it is applied when the formation water is characterized by presence of sulfate and bicarbonate ions in high concentrations that the calcium ion may lead to precipitation. NaBr is used alternatively to calcium brine; the density range is from 8.4 lb/gal to 12.8 lb/gal. To increase density till the maximum by adding and mixing with NaCl. pH is 7.0, TCT 0°C (33°F) and turbidity lower than 3 NTU. This type of brine is more expensive in comparison with other brines because it is consistent with water and other formation liquids.

Sodium Bromide is applied for wells characterized by low TCT values and also in case when chloride-free brines are needed. In contact with calcium base brine such

compounds as bicarbonate, carbonate and sulfate precipitate and this prevents the potential formation damage to happen.

To make 1 bbl (42 gal) of Sodium Chloride/Sodium Bromide Brine (based on 95% NaBr and 100% NaCl):

Density at 70°F (lb/gal)	H2O (bbl)	NaCl (lb)	NaBr (lb)	Freezing Point (°F)
10.0	0.886	119.0	0	+30
10.5	0.871	89.6	46.4	19
11.0	0.856	69.3	92.3	5
11.5	0.841	48.8	139.0	-12
12.0	0.826	28.5	186.0	-3 TCT
12.5	0.812	8.1	232.0	+31 TCT
12.7	0.806	0	251.0	+45 TCT

Table 4. Components to make Sodium Chloride/Bromide Brine

Potassium Chloride KCl solution – it is a single-salt brine with a density range from 8.4 lb/gal to 9.7 lb/gal and used to hinder shale. KCl concentration of 2% and 7% can be added in clear-water completion fluid. Potassium chloride brines are characterized by TCT of 59°F (14.9°C) and NTU value lower than 3. Completion operations require shale stabilization in clay-sandstone, shale or clay formations, so this type of brine is used in other brine systems to improve inhibition of shale, it is shale/clay stabilizer in formations which are water-sensitive.

Physical properties:

Appearance	Colorless, odorless liquid
pH	6 to 9
Specific gravity	1.007 – 1.163 @60°F (15.5°C)
Crystallization temperature	14°F - 60°F

Table 5. Physical properties of KCl

Ammonium Chloride (NH<sub>4</sub>Cl) 99% – it is 99% purity dry salt and used as an additive, weight material which increases completion fluid's density ranging from 8.4 lb/gal up to 8.9 lb/gal. Chemically it is acidic and prevents or minimizes the damage of formation. NH<sub>4</sub>Cl solution is compatible with most types of formation

water and it is shale inhibitive. It is an effective clay stabilizer and hinders damage of formation after an acid treatment.

Ammonium chloride is applied to fresh water by means of the rig hopper during agitating until all crystals are dissolved. While mixing the endothermic reaction occurs, therefore fluid temperature decreases.

Physical properties:

Appearance	Colorless, odorless crystals
pH	5 @10 wt%
Specific gravity	1.53
Water Solubility	24% @45°F

Table 6. Physical properties of NH<sub>4</sub>Cl

- Divalent Brines

Calcium Chloride CaCl<sub>2</sub> – it is formed from liquid or dry stocks, single salt blend. The properties characterizing this type of brine are: TCT of 1.1°C (34°F), densities from 9.0 lb/gal up to 11.6 lb/gal. To achieve densities of higher values it can be mixed with heavier brines. Divalent solution CaCl<sub>2</sub> is highly economical brine system and it is applied as a single-salt brine in order to inhibit clay dispersion, migration and swelling.

To prepare 1 bbl (42 gal) of Calcium Chlorine brine (based on 95% CaCl<sub>2</sub>):

Density at 70°F (lb/gal)	CaCl <sub>2</sub> (%)	H <sub>2</sub> O (bbl)	CaCl <sub>2</sub> (lb)	Freezing Point (°F)
8.4	0.9	0.999	3.2	+31
8.5	2.2	0.996	8.1	20
9.0	8.8	0.979	35.1	21
9.5	15.2	0.956	64.0	9
10.0	21.2	0.931	93.9	-8
10.5	26.7	0.906	123.8	-36
11.0	31.8	0.877	154.8	-22 TCT
11.5	36.7	0.846	186.6	+28 TCT
11.6	37.6	0.840	193.0	+35 TCT
11.8	39.4	0.828	205.5	+55 TCT

Table 7. Components required to prepare Calcium Chloride Brine

TCT is thermodynamic crystallization temperature.

Disadvantage: divalent brine is highly exothermic and hygroscopic in the case, if it is mixed with water the temperature can increase up to 93.3°C (200°F). Therefore, personal protective equipment must be provided.

Physical properties:

Appearance	Colorless
pH	6.0 – 10.5
Specific gravity	1.0 to 1.391 @60°F (15.5°C)
Crystallization temperature	From -59° to 44°F (-50° to 7°C)

Table 8. Physical properties of CaCl<sub>2</sub>

Calcium Chloride Solution 11.6 – is a single salt blend 38% by weight calcium chloride solution which is exploited as a completion fluid. It can be added as a component in a multi-salt mixture or individually to form a single-salt brine.

It is characterized by inhibitive features preventing swelling clays' migration and hydration; by ability to be mixed with different clear brines to get desired crystallization temperature and specific gravity. This solution is compatible with most of oilfield elastomers.

Physical properties:

Appearance	Colorless
pH	6.0 – 8.0
Specific gravity	1.391 @60°F (15.5°C)
Crystallization temperature	44°F

Table 9. Physical properties of CaCl<sub>2</sub> (11.6)

Calcium Bromide CaBr<sub>2</sub> – it is single-salt brine prepared from a dry or liquid stock materials. This blend is prepared from fresh water, 14.2 lb/gal stock fluid (calcium bromide 14.2) and calcium bromide solid. The standard density range is from 8.4 lb/gal up to 15.1 lb/gal. The maximum density can be reached is 15.5 lb/gal. The most appropriate environment is characterized by cold climate. CaBr<sub>2</sub> is characterized by -18°C (0°F) and TCT of low values.

Calcium bromide brine ensures a great inhibition, hinders clay migration and hydrating, may be applied like a packer liquid. So, it is characterized by inhibitive abilities and reduces damage of formation which can be induced by clay dispersion and swelling. To regulate the density, it can be added to the other brines. It needs to be treated attentively because it may cause the same problems as CaCl<sub>2</sub>.

Physical properties:

Appearance	From colorless to straw colored
pH	6.0 – 8.0
Specific gravity	1.008 to 1.81 @60°F
Crystallization temperature	-96°F to 66°F (-71°C to 18.9°C)

Table 10. Physical properties of CaBr<sub>2</sub>

14.2 Calcium Bromide – it is a single blend. 14.2 pound per gallon calcium bromide is applied as a completion fluid. It may be used as a component of multi-salt mixture or as a single salt; also, can be used like a spike fluid in order to increase density. It is suitable in use with the most of oilfield elastomers.

Physical properties:

Appearance	From colorless up to straw colored
pH	6.0 – 8.0
Specific gravity	1.70 @70°F (21°C)
Crystallization temperature	10°F

Table 11. Physical properties of 14.2 Calcium Bromide

Calcium Chloride/Calcium Bromide/Zinc Bromide CaCl<sub>2</sub>/CaBr<sub>2</sub>/ZnBr<sub>2</sub> – it is high density multi-salt heavy solution, prepared by mixing calcium bromide/chloride with zinc bromide in order to adjust and get required density and TCT. The density interval is between 14.0 lb/gal and 19.2 lb/gal. So, this blend is exploited when high density values are needed. It is prepared by mixing 19.2 lb/gal Calcium/Zinc Bromide, 14.2 ppg Calcium Bromide and Dry Calcium Chloride.

This blend is characterized by properties such as pH range 1.8-6.0, turbidity value lower than 5 NTU. It is highly compatible with Zinc/Calcium Brines and water.

It is applied for the completion operations where high density is required and mostly in cold climate environments. This brine hinders formation clay migration and swelling. This mixture is exploited also as a packer fluid and may be blended with a broad TCTs range. It is compatible with the most of oilfield elastomers, except nitriles.

Physical properties:

Appearance	Clear amber liquid
pH	Lower than 4.0
Specific gravity	1.8 up to 2.30 @60°F
Crystallization temperature	Depends on formulation

Table 12. Physical properties of CaCl<sub>2</sub>/CaBr<sub>2</sub>/ ZnBr<sub>2</sub>

Calcium Chloride/Bromide solution – clear brine, which is used as a completion fluid, it is prepared from 11.6 lb/gal chloride solution, dry calcium chloride and 14.2 lb/gal calcium bromide. The density range is from 11.6 lb/gal to 15.1 lb/gal.

Physical properties:

Appearance	From colorless to lightly yellow fluid
pH	6.0 – 8.0
Density	11.6 lb/gal to 15.1 lb/gal
Specific gravity	1.39 – 1.81
Crystallization temperature	60°F (maximum)

Table 13. Physical properties of Calcium Chloride/Bromide mixture

Calcium/Zinc Bromide solution – two-salt blend (CaBr<sub>2</sub>/ZnBr<sub>2</sub>) which is used as a completion fluid and it is characterized by densities from 15.0 lb/gal up to 19.2 lb/gal. These types of brines are prepared from dry calcium bromide, calcium/zinc bromide and 14.2 ppg calcium bromide. They are characterized by inhibitive features preventing migration and hydration of swelling clays.

Physical properties:

Appearance	Clear amber fluid
pH	Lower than 4.0
Specific gravity	1.8 to 2.30 @60°F (15.5°C)
Density	15.0 to 19.2 lb/gal @60°F
Crystallization temperature	Depends on formulation

Table 14. Physical properties of Calcium/Zinc Bromide

19.2 Calcium/Zinc Bromide – multi-salt clear solids-free blend (two-salt solution) characterized by the density of 19.2 pounds per gallon. Calcium bromide and calcium chloride are typically used in order to formulate the blend with different crystallization temperatures and densities. This type of mixture may also be used as a spike fluid in clear brines. Except nitriles, the most of oilfield elastomers are compatible with it.

Physical properties:

Appearance	From clear to amber fluid
pH	Lower than 4.0
Specific gravity	2.30 @60°F (15.5°C)
Density	19.2 lb/gal @60°F
Crystallization temperature	16°F

Table 15. Physical properties of 19.2 Calcium/Zinc Bromide

### 2.1.2 Clear Brine Fluids – Formates

Another type of special innovative brines is formate. Formates are monovalent, they are produced from formic organic acid. Sodium hydroxide, cesium hydroxide or potassium hydroxide react with formic acid in order to get solids-free potassium formate, sodium formate and cesium formate brines. Halides are not compatible with formates.

Single-salt Formate Blends are made of one salt. Densities are varying slightly above the water density, from 8.4 ppg sodium formate to 19.2 lb/gal cesium formate brine.

Sodium Formate (NaCOOH) – it is exploited as a solids-free completion fluid and can be made by mixing drill water with dry sack material or like a stock fluid. The density range is from 8.4 lb/gal to 11.0 lb/gal. This type of brine may be used instead of chloride base or calcium base brines. NaHCO<sub>2</sub> is characterized by pH equal to 8.6, plastic viscosity of 29 cP (40 wt% solution) and NTU value lower than 3.

NaCOOH is applied to decrease impact of shale and clay migration and inhibition. There is no precipitation and blocking or damaging the reservoir formation because the brine is not reacting with bicarbonates, sulfate or carbonates ions. In order to decrease the price this brine can be mixed with potassium formate.

Potassium Formate KCOOH – this brine is alternative to chloride and bromide brines. It is less hazardous, causing less safety, health and environment risks, therefore more expensive in comparison with single-salt brines. It is prepared from liquid stock or dry sack material. The density values are from 8.4 lb/gal up to 13.1 lb/gal. KCOOH brines guarantee better clay stabilization and improved thermal stability. Potassium formate can dissolve barium sulfate at high temperatures. Saturated potassium formate is highly lubricious and guarantees good hydrate inhibition.

Cesium Formate (CsCOOH) – is applied when required fluid densities should be above 13.2 lb/gal. The maximum density of this brine is 19.2 lb/gal.

Multi-salt blends are made of two or more formates. The purpose of mixing several blends is to get required density and crystallization temperature (TCT), pressurized crystallization temperature (PCT) with the lowest price. However, not economic potassium, cesium and sodium formates can be mixed together.

Potassium/Sodium Formate (KCOOH/NaCOOH) mixture - Potassium and Sodium Formates are blended with densities range from 11.0 lb/gal up to 13.1 lb/gal. Mixtures made at densities lower than 11.0 lb/gal are applied when low TCTs values and additional shale inhibition are required.

Cesium/Potassium Formate (CsCOOH/KCOOH) mixture – Cesium and Potassium Formates are characterized by density ranges from 13.1 lb/gal up to 19.2 lb/gal. They are blended in order to get desired density and PCT/TCT. Mixing the potassium and cesium formate also lowers the cost.

So, some features can be highlighted. There are various brines used as completion fluids at low to moderate pressures and low to medium temperatures. High density completion fluids often above 16.7 ppg (2.0 s.g) are used in the case of higher pressures. Zinc bromide ( $ZnBr_2$ ) and Cesium Formate (CsCOOH) are two high density brines available in the oilfield. pH of zinc bromide is near 2 which is highly corrosive and may cause safety hazards on the rig. It is no longer used in the North

Sea, as it is priority pollutant. Cesium formate is environmentally acceptable slightly alkaline brine which is less corrosive and widely used in the HPHT wells.

The cesium formate brines are preferred HPHT completion fluids in the environments characterized by temperatures up to 235°C (455°F) for 6 months and 180°C (356°F) for 24 months period which is highly compatible to be used in the North Sea environment.

One of the zinc bromide brine application disadvantages is it is used with adding of a corrosion inhibitor thiocyanate-based which at the moderate temperatures decomposes to H<sub>2</sub>S.

The cesium formate includes the formate ion which is an organic ion under a certain high-temperature conditions and over time can decompose and evolve hydrogen gas. Cesium formate showed a good performance under HPHT conditions, however in XHPHT (extremely high pressures and higher temperatures) wells there are some concerns about using this brine. In order to address this issue cesium acetate has been developed as an alternative completion brine to use in the XHPHT wells. As cesium formate the cesium acetate has the same beneficial properties and features as it is slightly alkaline which is compatible with bicarbonate/carbonate pH buffer and it does not include halide ions, one of the prior contributors to SCC (stress corrosion cracking) and pitting. The benefit is that the acetate ion is much more stable to much higher temperature in comparison with the formate ion. An extensive corrosion testing program has been carried out over the past 3 years to define cesium acetate efficiency to use in completion fluids for XHPHT wells. A number of austenitic alloys and martensitic duplex have been carried out to the brine for periods of maximum 6 months without and with the presence of acid reservoir gases and at maximum temperatures up to 232°C (450°F).

The experiments determined that cesium acetate does not lead to any of the known HPHT corrosion issues like hydrogen charging of duplex and austenitic alloys, stress corrosion cracking (SCC). As a conclusion of the tests is that cesium acetate proves

to be highly effective completion fluid for XHPHT wells on the basis of corrosion testing.

Cesium Acetate (CH<sub>3</sub>COOCs) – a salt of acetic acid and cesium hydroxide used to achieve completion fluids of high-density. This salt is characterized by neutrality to the alkaline pH in water-based solutions and, in comparison with the cesium formate, it has higher temperature stability.

Another type of additive used in completion fluids in order to enhance their performance is Carboxymethyl Starch (CMS) which is derivative of a natural starch. CMS is used first of all in the completion fluids in order to control the fluid-losses. It can be affected by electrolytes and hardness present in the brine solutions because carboxymethyl starch is slightly anionic.

Carboxymethyl Starch (CMS) in the approach of manufacture and various types of uses is similar to the Carboxymethylcellulose (CMC). The branched and linear starch polymers react in alkaline solution with monochloroacetic acid, adding at the OH positions carbomethyl groups by an ether linkage. By means of CM groups addition the starch reaches more resistance to the bacterial attack and thermal degradation.

Carboxymethyl Hydroxyethylcellulose – a cellulose polymer which includes nonionic hydroxyethyl and anionic carboxymethyl groups supplemented by ether linkages on the cellulose backbone to the OHs. It is widely used in completion fluids and brines.

M-I SWACO company offers minimally damaging clear-brine completion fluids which are prepared under distinct specifications such as certain densities, clarity, PCT (pressure/temperature freeze points), TCT (freeze points). Among these fluids there are formate and halide brine solutions.

**Ammonium chloride** (dry) – is a clay and shale inhibitor and is suitable for low-density operations.

**Calcium bromide** (dry/liquid) – it is used to inhibit migration and hydration of swelling clays. It exists in different variations: as a zinc bromide/calcium bromide blend, calcium bromide/calcium chloride blend.

**Calcium chloride** (dry/liquid) – decreases formation damage induced by clay swelling and solids, solids and clays migration or dispersion.

**Potassium chloride** (dry/liquid) – used to stabilize shale in clay-containing sandstones, shale formation and water-sensitive clay.

**Sodium bromide** (dry/liquid) – prevents potential of formation damage through sulfate, bicarbonate and carbonate compounds. Exists also as a sodium chloride/sodium bromide.

**Sodium chloride** (dry/liquid) – used in shallow-pressure wells for low-density operations, which do not require inhibitive features of potassium or calcium systems.

As density of brines increases, they become more harmful. Exposure of brines can be a reason of eye damage or skin irritation. Sodium bromide and sodium/potassium chloride are medium irritating, while calcium bromide, calcium chloride and zinc bromide are highly hazardous with the possibility to blind and induce blistering of the skin alike as a burn.

## **2.2 Application of cesium/potassium formate in Kvitebjørn, North Sea Field, Statoil**

Kvitebjørn is a high-pressure high-temperature (HPHT) gas/condensate field characterized with pressure of 81 MPa/ 11,700 psi and temperature equal to 155°C/311°F. Fourteen sections of HPHT reservoir has been drilled and twelve of them completed with potassium/cesium formate brine since 2004. One of the wells was completed in 12.7 days. Based on the performance of cesium formate brine in the Kvitebjørn field some conclusions were made. The wells production is maximized while formation damage risk is minimized. The well control was also improved. Low-solids cesium formate brine provided excellent well control in comparison with traditional water-based, oil-based solids-laden fluids. As it was

observed during drill-in and completion operations high-density solids-free cesium formate provided fast, efficient and safe operations.

The following benefits were observed during the application of cesium formate brine in the field:

- 1) No sag-related problems due to elimination of weighting solids.
- 2) Reduced risks of losses, kicks and destabilization as low gel strengths and no solids provide reduced surge/swab pressures.
- 3) Wells with narrow windows between fracture and pore pressure gradient are safely drilled without using managed pressure drilling or other costly techniques because of Low ECDs.
- 4) Low solubility of reservoir gases in the formate fluids provides early kick detection.
- 5) Cesium formate brine is characterized by hydrate-inhibiting properties which provide low risks of hydrate plugging.
- 6) Cesium formate brines allow overbalanced completions.
- 7) During circulation breaks virtual elimination of gas diffusion inside the high-angle wells.
- 8) Due to low solids amount inside the fluids, effective reliable operation of isolation valves is provided.

### **2.3 Application of cesium/potassium formate in the Martin Linge HPHT field of North Sea, Total E&P**

First three gas wells experienced difficult cleanup in the Martin Linge HPHT field. For the fourth well it was decided to pass from OBM to cesium formate fluid. Production index doubled in comparison with first three wells, a fast cleanup/production test was done and verified it. Also rate of penetration (ROP) enhanced significantly. There were no limitations set for ROP, however it was kept under control lower than 15 m/hr in shales and approximately 5 m/hr for pay-zones to control torque and gas levels. For this reason, the same kind of bit with a startling decrease of 56% in weight on the bit was used. The overall stress of the open hole

was reduced due to the use of cesium/potassium formate completion fluid which is characterized by optimized rheology.

According to the results of cesium/potassium formate application in the Martin Linge field, there are several benefits of the use:

- 1) Faster drilling operation
- 2) Significant improvement of hole stability
- 3) High operation efficiency
- 4) Superior hole cleaning
- 5) PI doubling in comparison to the first three wells

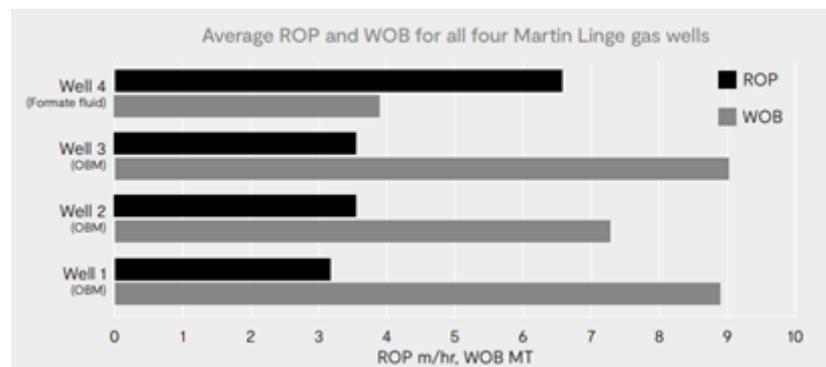


Figure 8. ROP increased significantly despite the low WOB due to application of cesium/potassium formate.

#### 2.4 Application of cesium/potassium formate in Huldra, North Sea field, Statoil

Cesium formate was used in this gas/condensate field to drill and complete 8 1/2" reservoir sections comprising six wells. The wells were drilled through reservoir at inclination 45° to 55° and completed in openhole. Upper completions were run in clear cesium formate brine and lower completions in the drilling fluid.

For the first Huldra well oil-based mud was applied as a reservoir drill-in fluid, however, while running sand screens a severe kick was met. According to this problem Statoil drill and completed the remaining sections of reservoir with the use

of cesium formate fluid. Consequently, enhanced kick detection with better well control and enhanced production were achieved.

Benefits observed by Statoil are:

- 1) low ECDs
- 2) increased trip speed
- 3) great well control
- 4) avoided swab and surge
- 5) improved hole cleaning
- 6) reduced time for flow checks

## **2.5 Safety, Health and Environmental Risks**

As all chemicals brine systems are dangerous and require careful handling. Brines are made of salts which are dissolved in water and therefore they are providing weight due to the solved salt quantity. As the density increases (heavy brines) the hazards for environment and equipment become much more significant.

Different properties which characterize blends with whatever weight:

- 1) Level of toxicity
- 2) Acidity (pH value)
- 3) Water absorption
- 4) Chemical interaction

PPE (personal protective equipment) must be provided and used in order to be in safe from the effects if exposure will happen when brine is mixed and applied.

## **2.6 Viscous brines**

In order to avoid different disadvantages of acidizing filter cakes viscous brines are used. The brines are thickened up to higher viscosities (several hundred cP) by means of hydroxyethyl cellulose (HEC) in order to limit invasion inside the formation. Bridging agents are not contained in the viscous brines. Also, no positive

shut-off and no external filter cake are obtained. Due to the high viscosity the rate of invasion is decreased. In some cases, according to Scheuerman, to obtain needed viscosity, a minimum of 4.2 lb/gal (12 kg/m<sup>3</sup>) HEC can be required. Practically, a viscous brine's pill is spotted above or throughout the loss zone perforations. In order to penetrate into the zone at least three feet the volume of pill must be sufficient. The pill must be mixed with a viscosity breaker to prevent the backflow out of the formation at the end of the work. Mostly used HEC breakers are effective in a few hours up to the day or only for short-term applications. Low viscosity HEC liquids may induce permeability damage when the polymer stays stable.

In order to use viscous pills to control seepage losses, is to use low density brine like medium one for the pill. Instead of spotted in the wellbore the low-density viscous brine is squeezed inside the formation. Which allows, without pressure control problems, to be used in the presence of high-density brine systems. For extremely permeable zones a crosslinkable HEC polymer is used to prevent seepage loss.

If the density of brine is greater than 12 lb/gal (1.4 SG) HEC becomes slower in developing brine viscosity. In order to achieve maximum viscosity five hours of mixing time may be required even when heated the mixture. This behavior is induced by the hydration of zinc and calcium ions change the water solvation energy in such manner that HEC does not yield till it is heated.

In the field HEC is used in the heavy brines firstly by prehydrating the polymer in an inert solvent like isopropyl alcohol, then adding and mixing it in the brine. This procedure has the same effect as heat. HEC will not yield when prehydrated or heated in some brines which contain zinc. In this case the zinc amount must be increased till sufficient concentration and consequently the solvent will be able to solvate the prehydrated HEC. The minimum needed zinc concentration is about 7.5% - 9.0% by weight.

There are several brines which are commonly used as completion fluids and their density ranges represented in the next table:

<b>Brine composition</b>	<b>Density range, lb/gal</b>
KCl	8.3-9.7
NaCl	8.3-10.0
CaCl <sub>2</sub>	8.3-11.8
NaCl/NaBr	10.0-12.7
CaCl <sub>2</sub> /CaBr <sub>2</sub>	11.8-15.2
CaCl <sub>2</sub> /CaBr <sub>2</sub> /ZnBr <sub>2</sub>	14.5-19.2
CaBr <sub>2</sub> /ZnBr <sub>2</sub>	14.2-21.0
ZnBr <sub>2</sub>	13.5-21.0

Table 16. Commonly used brines as completion fluids

## 2.7 Water-base fluids, containing oil-soluble organic particles

Completion fluids used in highly permeable zones may demand addition of bridging agents in order to prevent fluid loss. Oil-soluble organic particles, such as resins and waxes, are used in several types of fluids. In some conditions, as at low enough temperatures, these particles are deformable and act as bridging and filtration control agents. The most effective performance is shown at temperature range from 150°F up to 200°F (65°C-95°C). The particles become very soft at temperatures above 200°F and rigid at temperatures lower than 150°F. The organic particles comprise surfactants, wax and an ethylene-vinyl co-polymer. By means of these particles filter losses down to 24 cm<sup>3</sup> and to 7 cm<sup>3</sup> by addition of a chrome lignite can be obtained. With potassium chloride maximum density 10 lb/gal (1.20 SG) can be reached. In the system given and described by Crowe and Cryar the thermoplastic resin particles, which are highly deformable, are providing filter losses down to 7 cm<sup>3</sup> without the requirement in use of a supplementary agent. But for permeabilities of rocks higher than 900 mD this control is lost. The advantage is that the system is stable in all types of brines at maximum saturations. In another system described by Suman the thermoplastic resins are characterized by softening point of 182°C (360°F) and guarantee only bridging requirements, but do not provide filtration control. Polymers and starch derivatives ensure filtration control. Also, HEC is used to define carrying capacity. The system is stable in brines with high saturations at maximum temperatures 149°C (300°F).

### **3. Innovative High-Density Non-Zinc Solids-free Completion fluid (HDNZ)**

TETRA Technologies Innovation Group and Operations Personnel of TETRA's Houma and Fourchon facilities supported the new project about testing and developing an innovative completion fluid to be used for ultra-deep-water environments.

Traditional completion fluids are with the use of caesium or zinc bromide. But they have technical, economic and environmental limitations. An innovative HDNZ (high-density non-zinc) solids-free completion fluid are implemented to fulfill the requirements and challenges of deepwater environments. Fluid density range is from 14.5 lb/gal up to 15.4 lb/gal.

Nowadays, UDW (ultra-deepwater) environment and production requires fluid systems characterized by low crystallization temperatures (both True Crystallization Temperature TCT and Pressure Crystallization Temperature PCT) and high fluid densities without the need to use zinc bromide.

The primary criteria to establish non-formate and non-zinc completion fluids system is pressure crystallization temperatures of 30°F or lower at 15000 psi and the density range from 14.5 lb/gal up to 15.4 lb/gal. Different non-aqueous and aqueous solutions were tested and evaluated.

The solutions which passed the preliminary screening are further tested for thermal stability. The first experiment was made at temperature of 265°F and an optimal solution based on the results was selected. No thermal degradation of HDHZ system at this temperature was detected. As the heat is increasing further testing were made. So, at 300°F and 325°F no thermal decomposition was discovered.

#### **3.1 Testing of completion fluid compatibility with other fluids**

The innovative non-zinc completion fluid was tested in order to analyze the compatibility with tubulars, various fluids, elastomers and with the formation.

HDHZ completion fluid test with formation fluids: the compatibility test was carried out at ambient temperatures with the synthetic formation in the following ratios:

Ratios	System
25:75	Brine/formation water
50:50	Brine/formation water
75:25	Brine/formation water

Table 17. Proportions of innovative completion fluid and formation water

The mixture samples were vigorously shaken and left for 24 hours. A small concentration of sodium chloride precipitated in the similar amount compared to the expected one from calcium bromide solutions subjected to the formation water.

The same test was carried out with using samples of crude oil. High-density Non-zinc solids-free completion fluid was tested at ambient temperatures with following ratios:

Ratios	System
25:75	Brine/crude oil
50:50	Brine/crude oil
75:25	Brine/crude oil

Table 18. Proportions of completion fluid and crude oil

The mixtures were shaken to get an emulsion and let sit for four days duration. The mixture system is mixed with crude oil under same conditions as compared solution of calcium bromide. Some emulsion stability was obtained at lower concentrations of crude oil, however, higher concentrations created stable emulsions which after four days did not break.

The same test was carried out by using 0.5% emulsion preventer concentration at 180°F and ambient temperature. As a result, the presence of emulsion preventer induced a complete break during less than 24 hours at temperature of 180°F and at ambient temperature total break was obtained after 24 hours.

HDNZ test with control line fluids: the test of completion fluid HDNZ was performed with different control line fluids in order to evaluate compatibility. The following ratios were used:

Ratios	System
25:75	Brine/control line fluid
50:50	Brine/control line fluid
75:25	Brine/control line fluid

Table 19. Proportions of innovative completion fluid and crude oil

Then taken samples were strongly shaken and left for 72 hours. As soon as two fluids were mixed in all samples the presence of solids was obtained. Generated solids amount directly depends on the control line fluid amount which is present in the sample. Approximately after 30 minutes after agitation the precipitate floated to the top of sample. However, with light agitation it became easily redistributed into the liquid. This system behavior is similar to behavior of control line fluids mixed with calcium bromide under the same conditions.

HDNZ completion fluid test with synthetic oil-based mud: a novel completion fluid was tested also with synthetic oil-based mud (SBM) in order to evaluate compatibility. The test was carried out at ambient temperature with the following ratios:

Ratios	System
25:75	Brine/SBM
50:50	Brine/SBM
75:25	Brine/SBM

Table 20. Proportions of innovative completion fluid and synthetic-oil based mud

The fluids were allowed to sit for 17 hours after they were shaken properly.

Consequently, 75:25 brine/SBM mixture became segregated into 3 layers: a light hydrocarbon-based top layer, middle layer consisting of completion fluid and lower layer is dense which comprises settled barite.

The 50:50 blend stratified into two layers, where barite settled on the bottom, as it was expected.

The 25:75 brine/SBM mixture generated a stable homogeneous blend. The system performs the same behavior as the calcium bromide shows while mixing with synthetic oil-based mud at the same circumstances.

HDNZ completion fluid testing with SBM Base Oil: the base oil used in the synthetic oil-based mud is tested with the HDNZ completion fluid system at ambient temperatures with the following ratios:

Ratios	System
25:75	Brine/base oil
50:50	Brine/base oil
75:25	Brine/base oil

Table 21. Proportions of innovative completion fluid and base oil

The fluids were mixed vigorously and let sit for 24 hours. As expected, in all cases, the two fluids separated quickly.

HDNZ completion fluid testing with elastomers: the test was carried out in order to evaluate compatibility of HDNZ system with thermoplastics and elastomers and compare this performance with the same density conventional calcium/zinc bromide solution calcium bromide solution of 14.1 lb/gal density. The test was done with duration of 30 days and at temperature 265°F. Compatibility was identified by several parameters such as hardness, swelling, elongation at break and 50% modulus. All system behavior is similar to performance of calcium bromide/zinc bromide and calcium bromide solutions.

### 3.2 Corrosion

A variety of tubulars was used to test the HDNZ system. Environmentally Assisted Cracking (EAC) studies were carried out by using Q125, 13Cr and 15Cr materials and general corrosion studies were done by using Q125 metallurgy.

### 3.2.1 General corrosion study

This study was carried out in order to evaluate the performance of innovative HDNZ completion fluid in comparison to with conventional calcium/zinc bromide brine characterized by the same density. This system was studied by using both solutions containing a corrosion control agent and neat solution.

The test was carried out with durations of 7, 14 and 21 days at temperature of 265°F. Higher corrosion speed were obtained with the use of zinc/calcium bromide blend which is followed by the uninhibited HDNZ system. The best results were observed with the inhibited HDNZ completion fluid system. For the fully inhibited HDNZ system 21-day corrosion rates were very low at 0.17 mils/year.

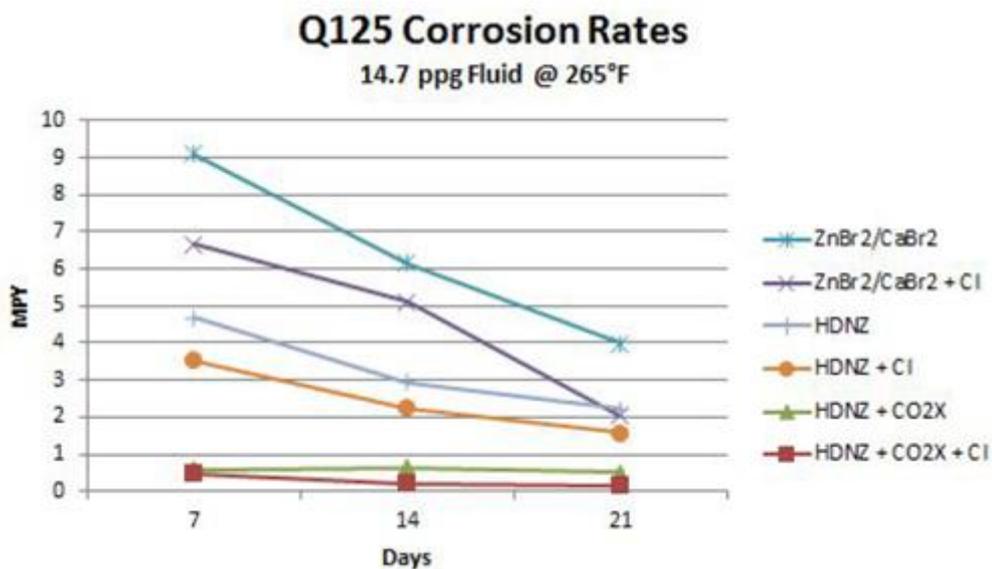


Figure 9. General corrosion rates depending on different brines

### 3.3 Study of Environmentally Assisted Cracking (EAC)

Environmentally Assisted Cracking (EAC) studies were carried out by means of using 13Cr, 15Cr and Q125 materials. The duration of test was 30 days at 265°F in a naturally deaerated environment: 30 psia CO<sub>2</sub>, N<sub>2</sub> up to 1000 psia. Tensile specimens were used for the Q125 samples and crevice specimens and C-Ring were used for the high alloy steels.

As a result, in the presence of the innovative high-density non-zinc completion fluid no cracking of 15Cr, 13Cr and Q125 metallurgies was obtained.

### **3.4 Testing to evaluate formation damage**

Return permeability testing was carried out in order to evaluate the behavior of the novel HDNZ completion fluid system and compare with the performance of conventional zinc/calcium bromide solution characterized by the same density.

Minerology and cores of comparable permeability were used for this study. The core samples were saturated by completion fluid and under confining pressure heated up to 265°F. Till permeability stabilized formation fluid was flowed in the direction of production. Then, in the injection direction 10 pore volumes of completion fluid were introduced and shut in for 60 minutes duration. Formation liquid was sent again in the direction of production and let flowing till permeability became re-stabilized.

The innovative HDNZ completion fluid system showed better performance comparing with zinc/calcium bromide brine, offering 60% of return permeability in comparison with the zinc/calcium bromide result of 41%.

### **3.5 Pressure and Temperature effects**

The high-density non-zinc completion fluid density, as with all clear brine fluids, as a function of pressure and temperature. The thermal expansion and pressure compression coefficients utilized in API Recommended Practice do not apply here due to the unique nature of the HDNZ system constituents. Different downhole density models were observed and then selected the model which offers a high level of correlation with field and experimental data.

### **3.6 Environmental compliance test**

This study was carried out in order to evaluate compatibility with North Sea and Gulf of Mexico (GOM) environmental regulations.

By using EPA Method 1617, Static Sheen and EPA Method 1664A, Oil and Grease, the system was tested to guarantee that HDNZ completion fluid can fulfill the Free Oil and Oil & Grease requirements of Section number 6 of The EPA NPDES permit

for GOM (Gulf of Mexico) discharges. As a consequence, the result under Method 1617 showed no static sheen and under Method 1664A less than 5 mg/L oil and grease, which demonstrates compatibility with the sections applicable of the NPDES permit like the Oil and Grease of Section 4 requirement (produced water) of the NPDES permit. Also, as the result, it was guaranteed not to comprise any main pollutants given in 40 CFR 401.1 and Section 307 of the Clean Water Act, which is fulfilling the requirement of Section 6 about Priority Pollutants of the EPA NPDES permit.

By means of using *Menidia beryllia* and *Mysidopsis bahia* populations according to EPA-821-R-02-014 methodology, both the high-density non-zinc innovative completion fluid and conventional 14.1 lb/gal calcium bromide brine were tested, 7-Day Toxicity test was carried out. The outcome of test showed that there was no significant toxicity difference between the 14.1 lb/gal calcium bromide solution and innovative HDNZ completion brine.

As a consequence, this type of completion fluid earned a Gold environmental rating due to excellent compatibility with North Sea environment regulations.

Performance of the system was observed in two wells of Gulf of Mexico. With the mudline temperatures of nearly 40°F the average water depth was in 7000 ft excess. The formation pressures were in excess of 21000 psi and BHT (bottom hole temperatures) were approximately 265°F.

### **3.7 Density**

With addition of 15.1 lb/gal HDNZ spike fluid and dry calcium bromide the surface densities were maintained. The system was highly hygroscopic due to the halide concentration amount. Therefore, weighting material frequent additions were required.

Yielding a bottom hole effective density of 14.49 lb/gal, so, predicted values were matched with the real downhole density.

### **3.8 Crystallization Temperature**

Both pressure crystallization temperature (PCT) and true crystallization temperature (TCT) met expectations and remained stable. The high-density non-zinc completion fluid was highly stable. As the result, PCT maintained values of 15000 psi at 30°F and TCT values range from 6°F up to 9°F with minor maintenance.

### **3.9 Compatibility**

The expectations about HDNZ system were met under field conditions. No major inconsistency with formation fluids was discovered. When the HDNZ completion fluid system encountered formation water influx there was minor NaCl salt precipitation. However, by means of normal filtration operations it was removed.

High-density non-zinc completion fluid is compatible with drilling fluids as well as calcium bromide brines and was reduced by use of effective displacement system design. The used systems of displacement were almost the same to those ones used with conventional systems. When exposed to control line fluids the performance of the system was alike with comparable calcium bromide solutions under same conditions.

In the case of elastomers there were no unforeseen compatibility problems. Under wellbore conditions in over 175 days of exposure, no issues of compatibility have been noticed. Also, related to corrosion study, no pitting, scaling or stress cracking corrosion (SCC) problems were induced by HDNZ completion fluid system with the 13Cr, Q125 and 15Cr materials at bottom hole temperatures range from 250°F up to 265°F.

The thermal stability testing showed no thermal decomposition was observed at bottom hole temperature of 265°F or at increased temperatures taken into account during perforating operations.

### **3.10 Workability and advantages of innovative completion fluids**

Different properties were observed during the field application and study. These criteria include displacement systems, filtration, sweeps, viscosity, fluid loss pills

and friction. Friction characteristics and viscosity of the innovative HDNZ were highly stable and fulfilled design criteria. Viscous sweeps and fluid loss control packages performed well in comparison to yield, temperature stability, yield time and serviceability, the polymer systems utilized in displacement systems.

The high-density non-zinc completion fluids were exploited like an integral component of the displacement system. No issues due to incompatibility with other system constituents were observed, and overall field performance criteria were fulfilled.

In addition to the HDNZ completion fluids standard high-capacity high-flow filtration systems were used and so, solids retention, flow rates and clarity met all expectations. The completion fluids characteristics were not affected by the filtration process and also, no impact was induced by addition of oil adsorption materials.

From the Health, Safety and Environmental (HSE) point of view the innovative HDNZ completion fluid system fulfilled all design criteria. No specific system problems related to environmental regulation compliance of GOM were observed.

**Advantages of innovative HDNZ completion fluid:**

- 1) The system is highly stable. There was no loss of density or attrition of properties for over six weeks while the fluid was stored on a workboat. The fluid was pumped out through over 20000 ft of wellbore and 7000 ft of riser. There is no a non-density-related effect on the crystallization temperature.
- 2) The system was subjected to different pressures and temperatures, however, there was no experienced loss of fluid characteristics.
- 3) All crystallization temperature requirements under the full range of operating circumstances were fulfilled by the HDNZ innovative system. It was used in order to test the BOP stack to over 14000 psi at temperature value less than 40°F.

#### **4. Development of a new high-performance brine-based completion fluid**

Several experiments were carried out for the purpose to design and develop characteristics of an innovative high-performance brine-based completion fluid to make it function properly under certain conditions. In order to formulate this innovative system sepiolite clay has been used. The samples properties were evaluated at temperature of 221°C and pressure differentials of maximum 300 psi to appreciate the effectiveness of a new viscosifier. The results of experiment showed that sepiolite based muds guarantee good rheological characteristics till 221°C in dynamic and static conditions with both Calcium bromide and Potassium formate brines. These types of muds yield better rheology by increasing salt amount and they are not sensitive to the intrusion of salt. So, these solutions can be used as a good alternative completion fluid especially for HTHP geothermal wells.

##### **4.1 Rheology**

Rheology of fluids is describing the deformation of their flow under applied stress. It is important, because rheology accounts for the non-Newtonian fluids' behavior. Viscosity is a parameter describing resistance performed by a flow of matter to a deforming force. Most of the viscosity is dominated by the shear. Any fluid's rheology involves following properties:

- Viscosity – it is a fluid's parameter which characterizes the relative movement among the two surfaces of liquid which have different velocities. So, in another words, viscosity is fluid molecules friction between each other. When the liquid flows through the tube, the particles near the tube's axis move more rapidly and near walls more slowly. Some pressure difference (stress) between tube's two ends is necessary to get over this friction and force the fluid to move. For a given velocity the liquid's viscosity and the stress are proportional. Penetration rate is affected by the viscosity at the bit, therefore when viscosity is lower the rate will be better. For instance, mud must be characterized by appropriate viscosity in order to lift the cuttings to the surface. So, viscosity is important parameter.

- Gel strength – as the fluid stays in static conditions for some time the time-dependent forces induce a viscosity increase. So, the gel strength is taking into account the electrochemical forces in the liquid at stationary conditions. This parameter depends on the solid contents, suspended solids, chemical composition, time and temperature. Usually, high concentration of clay induces it.
- Yield point – is a parameter characterizing the initial fluid flow resistance or it is a stress needed to make fluid to move. So, the attractive force among the colloidal particles is called yield point (YP). Another state is that YP is the shear stress which is extrapolated to a zero-shear rate, as for Bingham plastic model.
- Apparent viscosity – it is applied to a fluid shear stress divided by the shear rate. For non-Newtonian fluids the apparent viscosity is influenced by the shear rate, while for Newtonian fluid the apparent viscosity is constant and equal to the Newtonian fluid viscosity.

## 4.2 Viscosifiers

These viscosifiers will be used in the testing of completion fluids' properties change onwards.

- a) Sepiolite Nanoparticles – is a white soft clay mineral also called as meerschaum, often exploited for production of tobacco (or meerschaum) pipes. The chemical formula is  $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$  which is a complex magnesium silicate, it may be present in solid, fibrous and fine-particulate forms. This type of viscosifier is characterized by high porosity and low specific gravity, therefore it can float on the water surface. So, it is commonly found floating in the Black Sea and looks like sea-foam. It is widely used in oil industry, also used in lime mortars as a water reservoir. This viscosifier is off-white and opaque, cream or grey color, breaks with fine earthy or conchoidal fracture. The texture is fibrous. It can be scratched easily by nail. It is characterized by hardness equal to 2 on the Mohs scale and by specific

gravity range from 0.988 to 1.279. The mineral porosity may induce the error. Sepiolite is firstly soft, but then it hardens by solar heat or in a room with a warm climate.

Sepiolite is a clay mineral of sedimentary origin naturally occurring. It is a lightweight, porous, non-swelling clay characterized by a large surface area; its particles have a morphology which is needle-like. High porosity and specific surface area illustrate clay's absorption liquids capacity. Granules when they are saturated by fluids are not getting disintegrated.

Sepiolite-based additives affect viscous liquids by behavior called thixotropic which means that they are dispersed in liquid systems. The benefit of sepiolite suspensions, in comparison with other clays suspensions as bentonite, is that they are stable also in environment with the high ionic strength (high salt content). Clay sepiolite is used in oil industry because it is not sensitive for high temperatures, these properties are making this component valuable for a large range of uses. At high salinity and high temperature sepiolite suspension guarantees good rheological values.

The disadvantage is significantly high API water loss. Therefore, it requires rheological and filtration loss properties control while using it in drilling operations.

<b>Particle Structure</b>	<b>Fibrous</b>
Mohs' scale	2.0-2.5
Surface Area	150-320 m <sup>2</sup> /g
Cation Exchange Capacity	30-50 meq/100g
Melting Point	1550°C
Water Absorption	Wide
Oil Absorption	Up to 80% of its weight

Table 22. Characteristics of Sepiolite viscosifier

- b) XC Polymer (*Xanthomonas campestris* Polymer) - is a polysaccharide hidden by the genus *Xanthomonas campestris* bacteria another name of which is xanthan gum. This viscosifier guarantees highly desirable non-Newtonian

fluid rheology which is needed to lift cuttings in lower density liquids. Chemically XC is anionic with good tolerance for salinity and for hardness ions.

XC Polymer is powdered material, it may change in the number of bacteria debris residual and the ability of easy disperse in the water. Tolerance to temperature depends on the water-phase content, from 93° to 121°C (200°F to 250°F). XC polymer is not tolerated with extremely high pH values and hardness. This viscosifier is sensitive to bacterial attack. Large quantities of xanthan gum are exploited in oil industry in order to thicken muds. These liquids are used to take the solids back to the surface by the drilling bit. This viscosifier guarantees good 'low end' rheology. Some solids stay suspended in the fluid when the circulation stops. XC Polymer has a wide range of use such as in concrete poured underwater, etc., to prevent washout by increasing viscosity.

### **4.3 Testing innovative completion fluids with viscosifiers**

#### **4.3.1 Testing completion fluid with XCP viscosifier**

The experiment was carried out in order to discover if a basic Viscosifier is needed in the completion fluid. Xanthum Gum or XCP was applied at initial phase to appreciate the impact of viscosifier. Trimanganese tetraoxide (Micromax) was added to achieve preferential specific gravity. The temperature under 150°C is a suitable condition for XCP to perform a good efficiency and to have high yield points and viscosity. Micromax contributes to the specific gravity of the fluid specific gravity because itself this additive is characterized by sp.gravity of 4.8.

As a substrate potassium formate was used. The brine is characterized by an initial pH value of 8.7 and specific gravity of 1.562 (13.0111 ppg). Then, 600 ml of formate brine was blended with XC-Polymer of 0.3% w/v. It was mixed at a high shear rate and rpm with the duration of 25 minutes in a Hamilton-Beach mixer till the homogeneous solution is achieved. So, pH values and rheological parameters were measured. Also, specific gravity was evaluated by means of mud balance and retort

kit and obtained equal to 1.602. The well in Agartala Region requires the specific gravity of 1.63, so weighing component a.k.a Micromax was added. Then this mixture was again blended for 30 minutes more to get a homogenized smooth composition. So, to avoid any bubbles, lumps and granules. Further, pH, rheology and specific gravity were measured again. With addition of Micromax the pH value was increased, while apparent viscosity, yield point and plastic viscosity reduced before the hot rolling at temperature equal to 120°C for duration of 16 hrs according to API standards.

The blend was divided and poured into two cells and by the nitrogen gas under 100 psi pressurized and kept in a roller oven for hot rolling in dynamic conditions for 16 hrs. As 16 hrs passed, one cell was brought out from the oven, de-pressurized slowly and cooled till the room temperature. The properties such as specific gravity, pH and rheology were again measured. Another cell was left in the oven for additional 72 hrs with no change of the temperature in order to evaluate SAG factor.

In the cell of 16 hrs the fluid loss of composition was mentioned, which was stored on the top. So, to avoid this effect in the second cell of 72 hrs there was added a filtration aid Poly Anionic Cellulose (PAC). The parameters after PAC addition were again evaluated, the 72 hrs cell after the period ended was cooled at the room temperature, opened and depressurized. The mixture was filtered into four beakers separately. 20-25 ml at the top were registered as a clear fluid. Remaining amount was separated in three sections: bottom, middle and top segments. To obtain SAG factor the specific gravity of each section was evaluated.

#### **4.3.2 Testing Calcium Bromide with Sepiolite Viscosifier**

The experiment was done with Sepiolite clay nanoparticles of 6% as a viscosifier. Micromax (Trimanganese tetraoxide) was added as a weighing material to achieve required specific gravity value. Micromax's sp.gravity is 4.8. As a substrate Calcium Bromide was also added into the mixture. Brine is characterized by pH of 7.5 and specific gravity of 14.20 ppg (1.7055). The volume equal to 600 ml is blended with Sepiolite viscosifier 6% w/v. Then, in Hamilton-Beach mixer for 25 minutes at high

rpm and shear rate till when the homogeneous composition is reached. pH value and rheological parameters are measured. Also, by means of mud balance and retort kit specific gravity was obtained and is equal to 1.7212. To get higher value which is 2.1 Micromax weighing component was added to the mixture. Then for additional 30 minutes the mix was blended till to get homogenized smooth composition. In order to maintain required pH value 8.5 1mg of Lime was added. In order to avoid the corrosion in aging cell at HTHP 1 ml of Schlumberger Corrosion Inhibitor was also included. Results of new pH, specific gravity and rheology values were evaluated.

As a consequence, pH increased, but PV, YP and AV reduced before 220°C hot rolling for 16 hrs duration according to API standards. The composition was separated and filled into two aging cells, each of them has volume of 300 ml. Further step was pressurizing by nitrogen gas up to 300 psi and kept in a roller oven for the hot rolling in dynamic conditions for duration of 16 hrs at the temperature equal to 220°C. One of cells was brought out of the oven after 16 hrs, slowly de-pressurized and cooled at a room temperature. After that new values of pH, rheology and specific gravity of composition were obtained.

Another cell was not taken out, it was kept for additional 72 hrs with no temperature change in order to calculate SAG factor. After 72 hrs passed, in the same way, the cell was de-pressurized, opened and cooled at a room temperature. The composition was divided separately into 4 beakers. 20-25 ml at the top was observed as a clear fluid. The remaining mixture was separated into 3 sections: bottom, middle and top segments. To evaluate SAG factor the specific gravity was calculated for each segment individually.

SAG factor was obtained equal to 0.528 which is very similar to the API standards 0.522.

Data obtained from the testing of completion fluid Calcium Bromide with Sepiolite Viscosifier:

Component	Product	Mixing time (minutes)	Quantity	Completion fluid specific gravity achieved: 2.1 (2.1076)
Brine	CaBr <sub>2</sub>	0 min	600 ml	
Viscosifier	Sepiolite	25 min	36 gm (6% w/v)	
Weighing Material	Micromax	30 min	404 gm (67.33% w/v)	

Rheology taken at 65°C					Top	Middle	Bottom
	Brine	Brine with Sepiolite	Completion fluid	Completion fluid	Completion fluid		
	at R.T.	At ambient temperature	Before Hot rolled	After Hot rolled @220°C for 16 hrs	After Hot oven @220°C for 72 hrs		
pH	7.4	7.4/8.5	8.4	8.6	8.3		
Sp.gravity	1.7055	1.7212	1.91	2.068	1.878	1.893	2.1076
Θ - 600	-	13	33	29	24		
Θ - 300	-	8	24	19	17		
Θ - 200	-	7	19	15	14		
Θ - 100	-	5	13	10	11		
Θ - 6	-	3	7	4	6		
Θ - 3	-	2	6	3	5		
Gel-0	-	2	6	3	5		
Gel-10	-	4	7	7	8		
AV	-	6.5	16.5	14.5	12		
PV	-	5	9	10	7		
YP	-	3	15	9	10		

Table 23. Results obtained from testing Calcium Bromide with viscosifier

SAG factor analysis results for completion fluid with adding sepiolite:

	Physical Observation	Inference
Top	Was not able to observe clear fluid. The sample from the top of fluid in visual comparison looks like the original slurry.	SAG Factor obtained: 0.528
Middle	No significant distinction between middle and top fluid. Specific gravity slight minute change indicates change in layer.	

Bottom	Without any settling complete slurry form. Specific gravity slightly higher than the original mixture. Desirable SAG factor is reached.	
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Table 24. SAG factor evaluation results

#### 4.3.3 Testing Potassium Formate and Sepiolite Viscosifier

The test was done with the viscosifier Sepiolite clay nanoparticles of 6%. Micromax (sp.gravity of 4.8) was exploited as weighing component, to achieve target specific gravity. Potassium Formate was added to a mixture as a substrate brine. Brine is characterized by initial value of pH 8.5 and specific gravity equal to 1.56 (12.9948 ppg). The volume of brine 500 ml was blended with Sepiolite viscosifier 6% w/v. It was mixed in the Hamilton-Beach mixer for duration of 25 minutes at high shear rate and rpm till the mixture became homogeneous. pH and rheological parameters were evaluated, also by means of mud balance and retort kit specific gravity was calculated equal to 1.5832. Then, Micromax was added and helped to reach specific gravity of 1.98. The mixture was further mixed for additional 30 minutes to get smooth homogeneous composition. Again the measurements of pH, rheology and sp.gravity were taken. pH value increased because of Micromax addition, while plastic viscosity, yield point and apparent viscosity decreased previously to the hot rolling at temperature 220°C for the duration of 16 hrs according to the API standards. The composition was separated in two aging cells with volume of 300 ml and under 300 psi was pressurized by means of nitrogen gas. For 16 hrs they were kept in a roller oven for the hot rolling at temperature 220°C in dynamic conditions. One cell after 16 hrs was brought out from the oven, cooled and de-pressurized at the room temperature.

The pH and other parameters were measured. The other cell was further kept in the oven at the same temperature for additional 72 hrs in order to evaluate SAG factor. After that the cell was taken out and cooled. The composition was separated into four beakers. 20-25 ml from the top was registered as a clear fluid, the remaining part was divided into 3 segments: bottom, middle and top. To measure SAG factor

specific gravity was evaluated firstly. The obtained SAG factor is 0.5 which is close to required value of 0.522 according to the API standard.

Data obtained from the testing of completion fluid Potassium Formate and Sepiolite

Viscosifier:

Component	Product	Mixing time (minutes)	Quantity	Completion fluid specific gravity achieved: 1.98 (2.023)
Brine	KHCO <sub>2</sub>	0 min	500 ml	
Viscosifier	Sepiolite	25 min	30 gm (6% w/v)	
Weighing Material	Micromax	30 min	357.44 gm (71.488% w/v)	

Rheology taken at 65°C					Top	Middle	Bottom
	Brine	Brine with Sepiolite	Completion fluid	Completion fluid	Completion fluid		
	at R.T.	At ambient temperature	Before Hot rolled	After Hot rolled @220°C for 16 hrs	After Hot oven @220°C for 72 hrs		
pH	8.5	10.4	10.6	12.5	12.5		
Sp.gravity	1.56	1.5832	1.95	2.023	2.0093	2.0120	2.0238
Θ - 600	-	14	39	75	55		
Θ - 300	-	8	26	43	41		
Θ - 200	-	7	20	31	34		
Θ - 100	-	4	15	19	28		
Θ - 6	-	2	6	5	18		
Θ - 3	-	1	5	4	17		
Gel-0	-	1	6	4	12		
Gel-10	-	3	7	6			
AV	-	7	19.5	37.5	27.5		
PV	-	6	13	32	14		
YP	-	2	13	11	27		

Table 25. Results obtained from testing Potassium Formate with viscosifier

SAG factor analysis results for completion fluid with adding sepiolite:

	Physical Observation	Inference
Top	Was not able to obtain clear fluid. The sample from the top of fluid in visual comparison looks like the original slurry.	SAG Factor obtained: 0.522
Middle	No significant distinction between middle and top fluid. Specific gravity slight minute change indicates change in layer.	
Bottom	Without any settling complete slurry form. Specific gravity slightly higher than the original mixture. Desirable SAG factor is obtained.	

Table 26. SAG factor evaluation results

#### 4.4 Conclusion

So, from the passed experiments some evident effects were observed:

- 1) Mud aging period affects significantly the rheological parameters and slightly the water losses. But no aging effect on the clay sepiolite was observed by the API standard. Aging period must last at least 16 hrs to achieve improved rheological values.
- 2) The composition achieves the best rheological parameters and total performance as a result of aging cell autoclaving. Rheology measurements showed lowering because of the weighing material's rapid settling. Due to 16 hrs heating duration in dynamic conditions the sepiolite clay gets its viscosifier parameters and as a result successfully holds well the material. Therefore, it is giving improved values of pH, rheology and specific gravity.
- 3) Sepiolite muds perform high values of the gel strength. The yield point to plastic viscosity ratio (YP/PV) is nearly equal to 3 which represents rheological characteristics.
- 4) Sepiolite represents a good performance with both KHCO<sub>2</sub> and CaBr<sub>2</sub> brines in HTHP conditions. It provides improved high specific gravity and yield point values.

- 5) Formulations which were tested with brines and Sepiolite clay nanoparticles represented good results of SAG factor, in HTHP conditions defining their stability. So, this result of experiment proves to be an appropriate alternative viscosifier for completion fluids.
- 6) The current formulations were used at compositions of 6% w/v w.r.t brine, so for higher efficiency higher concentration may also be tested and used.

## **5. Study of Effect of Fibers on the Flow Behavior of Polymer Completion Fluids**

The use of fibers in the completion fluids helps to enhance the rheological characteristics and the plugging efficiency of production layer by completion fluid and minimize the damage of formation induced by the filtrate. Even so, there are few studies about the impact of different fibers on the completion fluids' rheological properties and flow behavior through the pores.

The polymer completion fluid contains polymer, water phase and plugging material. The plugging materials are short fibers and solid particles which are selected according to the formation leakage channel radius. The short fibers improve migration and suspending abilities of the solid particles. Also, they form inside the leakage channel the temporary plugging layer with the solid plugging particles meeting an existing pressure difference.

As the base solution the polymer xanthan gum solution (XC) was chosen. The solution is prepared by mixing fresh water and xanthan gum. The concentration of XC used in completion fluid is 0.3 wt% (the ratio of XC mass to water mass). Xanthan gum purity is in the range of 95%-99%.

Bamboo, carbon, polyester and polypropylene fibers were selected for research. The fibers in polymer completion fluids are applied to affect the rheological properties and completion fluid's carrying capacity and also to decrease operating costs the concentration of polymer base fluid may also be reduced.

### **5.1 Results and discussion**

The effect of fibers on the properties of polymer completion fluids can be influenced by flow pattern index 'n' and viscosity coefficient 'K'. The effects of fiber content on the "n" value and "K" value are evaluated and shown in the following figures:

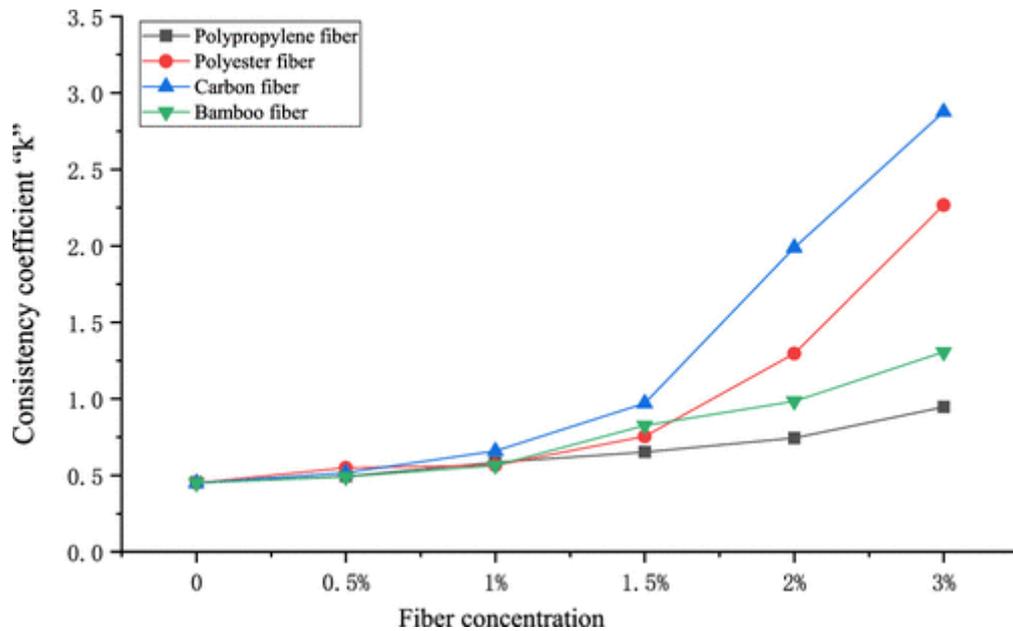


Figure 10. Effect of the fiber content on the “K” value at room temperature

As a result, with the increase of fiber concentration the viscosity coefficient “K” value increases and flow pattern index “n” decreases. The addition of fibers into the solution increases the viscosity of fibers suspension, increases the structural strength among solutions and improves suspension’s non-Newtonian property.

As it can be observed from the graph, “K” value starts to rise gently when the concentration of fibers is lower than 1.5 wt%. Further, the value of “K” rises sharply when the concentration achieves 1.5 wt%, because the contact opportunities among fibers grow significantly. Consequently, it leads to the thickening of polymer solution and improvement of interaction force of fiber structures.

The coefficient “K” is highest for carbon fiber, that means carbon fiber among the four kinds of fibers can strongly enhance polymer solution consistency. However, the amount of carbon fiber used must be controlled to avoid suspension from poor liquidity and from being highly thick.

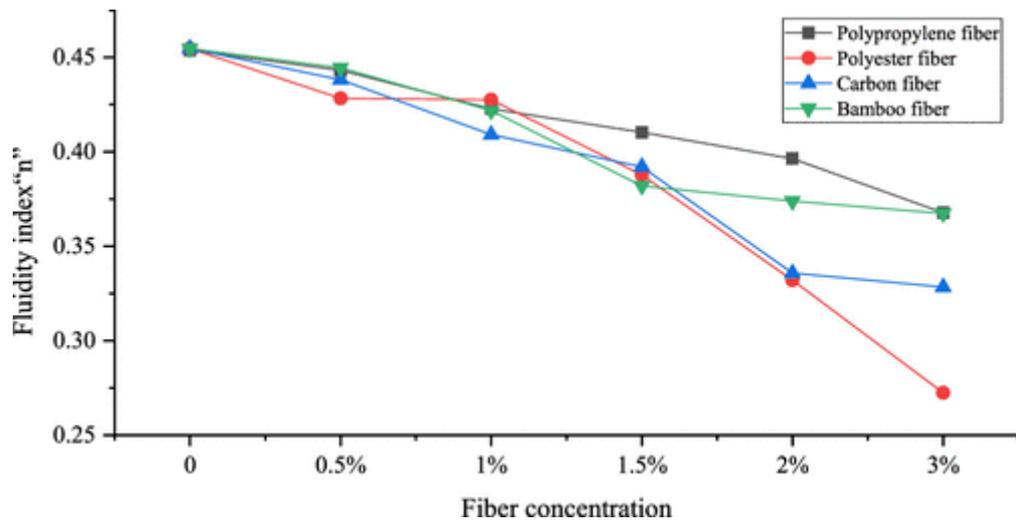


Figure 11. Effect of fiber addition on the “n” value at room temperature

The “n” value reduction enhances the carrying of plugging particles by suspension. As it can be observed from curves represented on the Figure 10, polyester fiber decreases fastest, consequently it is mostly favorable to enhance suspension non-Newtonian behavior. This means that polyester fiber addition helps to maintain efficient suspension state and carry solid particles better.

Generally, while using polyester fiber and carbon fiber in the polymer completion fluid, it is important to control the amount added to the fluid to avoid exceeding concentration which impact viscosity of completion fluid and so impacts downhole pumping. When bamboo fiber and polypropylene fiber are added in completion fluid, they do not highly influence rheological properties, therefore the amount of fiber can be increased to achieve good plugging performance of completion fluid.

## 5.2 The Flow Behavior of Fiber Suspension in Low-Permeability Pores

In the figure below it is shown completion fluid’s plugging scheme inside the pore channel of leakage formation. Fibers inside the completion fluid are existing as a three-dimensional dispersed phase. They are overlapped with each other and randomly distributed, so that twining and carrying the plugging particles inside the pore channels of different sizes.

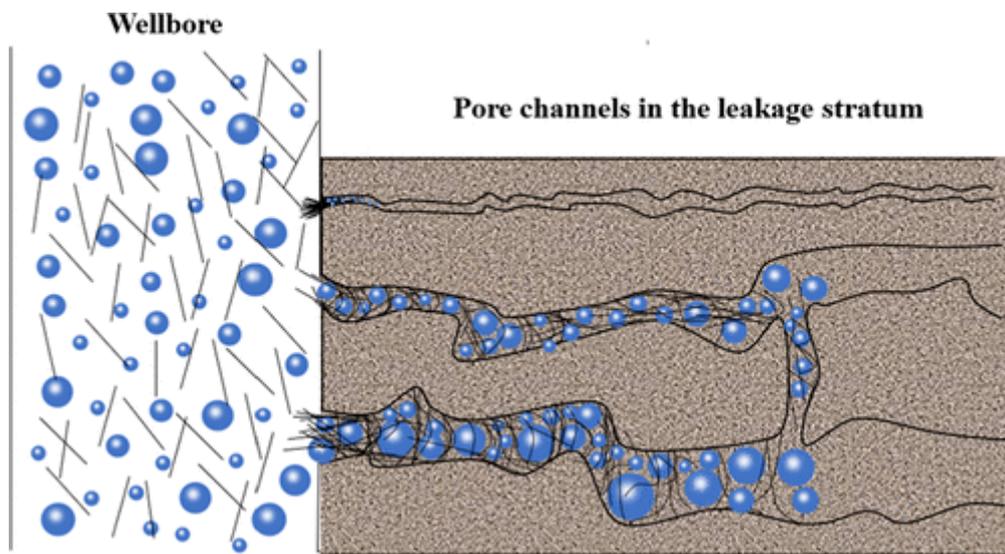


Figure 12. Plugging mechanism formed by solid particles and fiber in the pore channel of leakage formation.

Plugging particles and fibers are forming a plugging layer inside the channel. Under various flow conditions in pores completion fluid has a strong impact on the strength of plugging layer. In order to understand the flow behavior of completion fluid, the flow pattern in the pores was studied. The fluid behavior index “n” has a great impact on the settling velocity of proppant, which reduced as the Reynolds number increased. The flow core exists in the velocity profile similarly to the plastic fluid, as the completion fluid is a pseudoplastic fluid. The core size of completion fluid rises as the value of “n” reduces; therefore the flow shape changes to flat laminar flow from peak laminar flow.

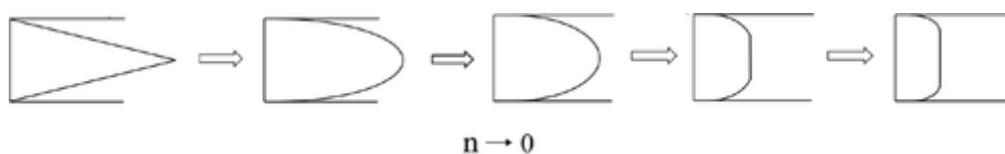


Figure 13. Relationship between the velocity profile and fluidity index n of pseudoplastic fluid.

As the polymer completion fluid goes inside the leakage formation, the fiber plugging particles become mostly effective, the particles enter the lost circulation formation as the fluid starts to be in flat laminar flow.

The variation of coefficient “n” can change the completion fluid’s flow state inside the pores. From the figure above it can be seen the relationship between fluidity index “n” and velocity profile of pseudoplastic fluid. Flat laminar flow can carry plugging particles at low velocity and viscosity for low solid polymer completion fluid. Consequently, the value of “n” must be controlled to improve the carrying capacity of solid particles.

Considering different temperatures, the flow behaviors of four different fiber suspensions were evaluated assuming the pore radius of 0.5 mm and the completion fluid flow velocity of 0.5 mm/s. As a result, the value of index “n” is in range 0.27 – 0.45. The value of “n” is smaller, as the fiber concentration increases. The flow pattern changes, so that the flow core size increases which leads to reduction of well wall erosion induced by fluid and achievement of better flow pattern.

Carbon fiber suspension is characterized by largest flow core size in comparison with other fiber suspensions, which means that this fiber is the most suitable for use as it is characterized by plate laminar flow.

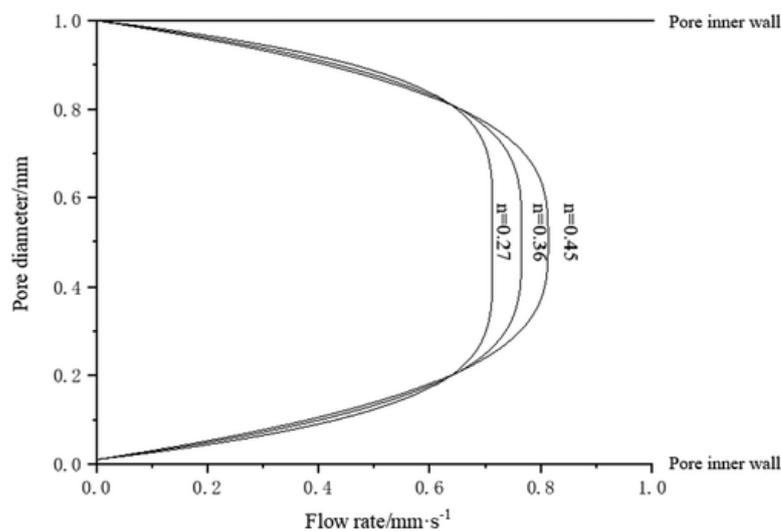


Figure 14. Effect of fiber concentration on the flow behavior of four kinds of fiber suspensions in pore space.

The flow pattern becomes sharper with the increase of temperature, which leads to unfavorable conditions for carrying the plugging particles inside the pores. The bamboo fiber flow core size is the largest, while polyester fiber is the smallest as the

temperature changes from 30 to 90 °C. Comparing all four kinds of fibers, the carbon fiber suspension shows the largest flow core size as the temperature increases.

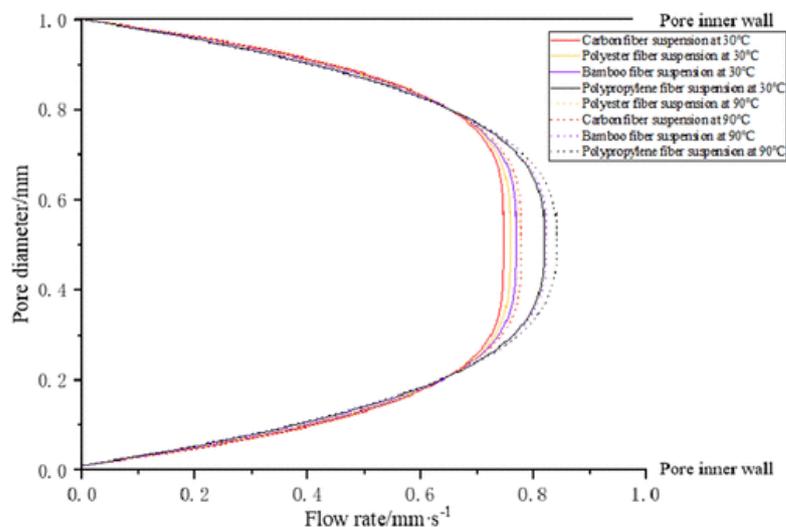


Figure 15. Flow behavior of different fiber suspensions in pores at 30 and 90°C.

### 5.3 Conclusions

1) Carbon fiber and polyester fiber strongly influence viscosity of polymer completion fluid. Polypropylene and bamboo fibers show little impact. If the fiber concentration is too high the viscosity of completion fluid rises sharply, therefore recommended fiber concentration is 2 wt%.

2) The use of fiber provides viscosity reduction of polymer completion fluid as the temperature increases in the range of 30–90 °C. Consequently, at a certain temperature, fibers ensure stability of completion fluid viscosity. Carbon fiber among four different fibers shows sensitivity to temperature rise. The suspension viscosity increases mostly as the temperature grows.

3) The carrying capacity and the flow behavior of polymer completion fluid are reflected by flow index “n”. The temperature, concentration and type of fiber highly affect the “n” coefficient. Carbon fiber and polyester fiber suspensions are characterized by flat flow patterns inside the pores, therefore they provide the most effective carrying performance for solid particles. As the “n” value and temperature increases, the carrying capacity of completion fluid worsens.

## **6. TETRA CS Neptune® innovative completion fluids**

The TETRA CS Neptune® innovative fluids are cost-effective, environmentally friendly alternatives to zinc brines and to cesium formates. Zinc brines are classified as marine pollutants and cesium formates are replaced zinc brines in the North Sea.

Cesium formates were used as an only existing solution to use in order to safely complete the wells. But now TETRA CS Neptune completion fluids meet all the requirements for sensitive environments. These types of fluids are made from renewable products without undissolved solids, zinc, formate ions or priority pollutants. These innovative completion fluids cause lower safety and health risks as they are neutral to alkaline pH. Their chemical composition is zinc-free, zero-discharge system is not required.

Zinc-Free, solids-free, Formate-Free Fluids are innovative high-density completion fluids from the TETRA CS Neptune family of fluids. There are monovalent and divalent completion fluids.

### **6.1 TETRA CS Neptune Innovative Monovalent completion fluids**

Monovalent brines are innovative fluids alternative to cesium formate and zinc bromides high-density completion fluids. They are used in completion and workover operations, also can be exploited as low-solids reservoir drill-in fluid (DIF). These type of completion fluids exhibit similar compatibility as sodium bromide with other reservoir and working liquids.

#### **6.1.1 Physical properties**

Monovalent solids-free, formate-free and zinc-free fluids are characterized by a density range from 12.4 to 15.7 lb/gal. They are characterized as odorless liquids soluble in water. pH range is from 7 to 10. The appearance is from clear to amber color. Monovalent salts may be used to ensure refined corrosion protection in comparison to alternative fluids. In the presence of sulfate ion-containing and carbonate formation fluids they can show low scaling tendencies.

<b>Physical properties</b>	
Density	12.4 to 15.7 lb/gal
pH	7-10
Water solubility	Soluble
Appearance	Clear to amber color
Odor	Odorless

Table 27. Characteristics of innovative TETRA CS monovalent completion brines

Monovalent innovative completion fluids can be designed up to 15.7 lb/gal without the use of formate salts with a true crystallization temperature (TCT) lower than 10°F (-12°C). They are stable during storage and at temperatures higher than 350°F (177°C). Monovalent liquids can be mixed with clear brines by means of mixing equipment. They are consistent with metallurgies and downhole elastomers.

### **6.1.2 Safety and Handling**

For safety reasons skin and eye contact, ingestion and inhalation must be avoided, personal protective equipment must be used. At the work station there must be adequate ventilation ensured. In the case if a proper ventilation is not available a specially designed respirator must be used. For more specific details Safety Data Sheet must be provided.

## **6.2 TETRA CS Neptune Innovative Divalent completion fluids**

Divalent completion fluids are high-density, zinc-free, solids-free, formate-free liquids for complex and offshore wells, including applications of high-temperature, which require the use of heavy clear brines during the completion phase in order to control well pressure.

The composition of Neptune Divalent fluids is made by using halide-based brines and a complex mixture of additives which reaches a large decrease in the TCT (true crystallization temperature) and PCT (pressure crystallization temperature) of the fluid. Each fluid is designed especially for TCT/PCT and density requirements of the project.

### **6.2.1 Physical properties**

The density range for divalent fluids is from 14.3 to 17.5 lb/gal. They can reach lower PCT and TCT than calcium bromide brines which have equivalent-density. These liquids are stable during storage and at high temperatures, are also characterized by good water solubility. pH range is 7-10.

<b>Physical properties</b>	
Appearance	Clear to amber liquid
Density	14.3 to 17.5 lb/gal
pH	7-10
Water solubility	Soluble
Odor	Odorless

Table 28. Characteristics of innovative TETRA CS divalent completion brine

There are several innovative completion fluids characterized by different properties shown in the following table:

<b>TETRA CS Neptune Innovative Completion Fluids Characteristics</b>	
TETRA CS Neptune Divalent Completion Fluids	Temperature stability up to 177°C/350°F Density up to 1.84 sg or 15.4 lb/gal Field proven
TETRA CS Neptune HDD Completion Fluids (High Density Divalent)	Temperature stability up to 143°C/290°F Reaches maximum density of 1.88 sg or 15.7 lb/gal Drill-in and low solids invert emulsions Pending or patents granted
TETRA CS NeptuneXHDD Completion fluids (Extra High Density Divalent)	Maximum density reaches 2.10 sg or 17.5 lb/gal
TETRA CS Neptune HDM Completion Fluids (High Density Monovalent)	Temperature stability up to > 177°C/350°F Density up to 1.57 sg or 13.1 lb/gal Drill-in, low solids invert emulsions and frac fluids Pending or patents granted
TETRA CS NeptuneXHDM Completion Fluids (Extra High Density Monovalent)	Temperature stability to > 177°C/350°F Density up to 1.88 sg or 15.7 lb/gal Drill-in, low solids invert emulsions and frac fluids

Table 29. Different types of innovative TETRA CS Neptune completion fluids

### **6.2.2 Safety and handling**

Divalent fluids cause health, safety and environment risks similar to calcium halide brines. Skin and eye contact, ingestion and inhalation must be avoided.

Advantages of Zinc-Free, Formate-Free Fluids:

- 1) Global environmental acceptability – for instance, North Sea has restricted zinc use. These new types of fluids are suitable, as they are zinc-free and so, no zero-discharge system is required.
- 2) Need for continuity of supply – TETRA CS Neptune fluids are made from renewable components, while cesium cost is corresponding to the depletion of sole commercially viable resources.
- 3) Unit price – TETRA CS Neptune innovative completion fluids are characterized by a lower unit cost than other completion fluids with the alternative chemistry composition.
- 4) Safety and health risks – minimized risks for both plant-based and rig-site personnel, as these fluids are characterized by a neutral pH.
- 5) Reservoir drill-in fluid – TETRA CS Neptune fluids can be used as drill-in fluids with composition of low-solids.
- 6) Ease of handling – these types of innovative fluids do not need any handling, special mixing, storage tank at the rig site.
- 7) Recyclability – by using standard technologies they can be recovered for reuse.

## 7. Innovative completion fluid components:

1) Micromax (weighing compound) – Trimanganese Tetraoxide or Micromax is an additive which increases density of a slurry with Hematite ground ore to a particle dimension in average of 5 microns. In comparison with the other weighing materials, Micromax when added and mixed in water it stays suspended in the mixture. Another type of additive is Micromax FF which has the same properties as the original Micromax, but it is much easier to handle. It can be mixed in dry condition, transferred pneumatically and the dust can be successfully reduced. The temperature range downhole which is suitable for use of this additive is from 27°C to 260°C (80°F to 500°F). For deeper wells characterized by higher temperatures weight additive Micromax may provide efficient mud displacement and sustain formation pressures. The slurry weight prepared individually for each well affects the additive concentrations.

№	Component	Example	Purpose
1.	Brine	CaCl <sub>2</sub> , KCl, NaCl, KHCO <sub>2</sub> , NaHCO <sub>2</sub> , CaBr <sub>2</sub> , CsHCO <sub>2</sub> , NaBr, KBr	Homogeneous mixing substrate
2.	Viscosifier	HEC, Bentonite, Attapulgate, Sepiolite, Saponite, Xanthan Gum	Improving completion fluid's holding capacity to support well completion
3.	Oxygen Scavenger	Na <sub>2</sub> S (Sodium Sulfide)	Decreases concentration of oxygen in the well and so inhibits corrosion to appear
4.	Corrosion inhibitor	Quaternary Ammonium Salt, Didecyl Dimethyl Ammonium Chloride	Forms a resistive layer which helps to prevent corrosive species interaction inside the well

5.	Defomer	Octanol (C <sub>8</sub> H <sub>18</sub> O)	Defomer is used to prevent foaming. A substance or polymer which significantly decreases the surface tension
6.	Weighing Material	Barite, Hematite, Trimanganese Tetraoxide (Micromax)	Enhances specific gravity

Table 30. Different components and additives

There are some common additives used in preparation of completion fluids:

Additive Types	Typical Compounds	Performed Functions
Breaker	Oxidizer, Acid, Enzyme breaker	Fluid viscosity reduction
Biocide	Glutaraldehyde carbonate	Bacteria inhibition
Buffer	Sodium bicarbonate	pH level control
Clay stabilizer	NH <sub>4</sub> Cl, KCl, KCl substitutes	Prevention of clay swelling
Diverting agents	Ball sealers, flake boric acid, rock salt	The fluid flow diversion
Fluid loss additive	Fine sand, Diesel, particulates	Enhances efficiency of fluid
Friction reducer	Anionic polymer	Hinders the friction
Surfactant	Nonionic, Fluorocarbon	Surface tension decrease

Table 31. Commonly used additives

## 7.1 Dry salts used in completion fluids

Dry salts weight materials are used in order to increase single salt fluid's density which has been diluted or to apply additional hydrostatic pressure which is needed to control the well.

Ammonium Chloride 99% (NH<sub>4</sub>Cl) salt – it is a dry salt of 99% purity, which is used as an additive to a completion fluid and when the ammonium ion is preferred as a gravel additive. NH<sub>4</sub>Cl is applied to increase completion fluids' densities and to prevent or reduce damage of formation, chemically it is acidic. Ammonium chloride is compatible with the most of formation waters and characterized by ability of shale inhibition.

When hydrofluoric (HF) acid (clay or mud acid) is used, NH<sub>4</sub>Cl hinders the insoluble fluorosilicates formation.

Advantages of ammonium chloride salt application:

- 1) May prevent migration and hydration of swelling clays due to inhibitive properties
- 2) In the certain environments it can be exploited to prevent precipitation and scaling issues
- 3) Compatibility with the most of oilfield elastomers

Before the use, formation water, fluid additives and other contacting liquids must be checked and screened for verification of compatibility with brines.

Physical properties:

Appearance	Colorless, odorless crystals
pH	5 @10 wt%
Specific gravity	1.53
Water solubility	24% @45°F

Table 32. Characteristics of NH<sub>4</sub>Cl 99% salt

Potassium Chloride 98% - is a weighting material, dry salt which is crystalline flowing powder of potassium chloride 98%. The purpose of usage is to formulate

and adjust density of completion fluids till 9.7 lb/gal. It is applied as a shale stabilizer in water-sensitive formations. Also, may be used in the mixture with other salts in order to improve inhibition.

The benefits: may prevent migration and hydration of swelling clays. In certain environments it may be used to prevent scaling and precipitation issues, compatible with oilfield elastomers. It is an effective shale/clay stabilizer additive in formations which are water-sensitive. It is used when the potassium ion is needed.

Before the use, formation water, fluid additives and other liquids must be checked for compatibility with brine. The solutions become saturated at 9.7 ppg (24% by weight). Potassium Chloride salt's dissolution rate reduces while the saturation is increasing, therefore heat and agitation may be needed in order to get a 9.7 ppg density.

Physical properties:

Appearance	White crystals, free flowing
pH	5.4 – 8.6 @5% solution
Specific gravity	1.98 @25°C
Water solubility	25.6% (wt) @20°C

Table 33. Characteristics of Potassium Chloride 98%

Potassium Chloride (KCl) salt – an effective shale/clay stabilizer additive in formations which are water-sensitive. It is used when the potassium ion is needed.

Sodium Chloride (NaCl) salt – widespread low-cost salt which is used to increase density, also by decreasing water activity it increases shale inhibition. It is characterized by the specific gravity of 2.165 and effectively reduces salt dissolution while drilling oil and gas wells with halite salt sections. Another purpose of application is to reduce the forming potential of gas hydrates. The maximum temperature at which NaCl can be applied is 260°C (500°F).

Sodium Bromide (NaBr) salt - when the chloride ion is not preferred, the sodium is desired instead of calcium, so the pure sodium bromide brine is used. When water

of formation contains high concentrate of carbonate or sulfate, NaBr is used, because calcium ion may cause precipitation.

Calcium Chloride (CaCl<sub>2</sub>) salt – is an economical additive used in completion fluids in order to inhibit clay dispersion, migration and swelling. For the most classes of cement calcium chloride is used as an accelerator.

Calcium Bromide (CaBr<sub>2</sub>) salt – used as a completion additive which increases density of calcium chloride, zinc bromide and calcium bromide brines. It is dry powdered inorganic salt composed of 95% calcium bromide. When chloride ion is not preferred calcium bromide is exploited. The benefit of calcium bromide salt application in comparison with calcium chloride is that it is characterized by effective higher density and in total less of the growth in the crystallization temperature per pound of added material. The calcium bromide is exploited when the zinc-based compositions are forbidden to use for the density range from 14.0 lb/gal up to 15.0 lb/gal.

Physical properties:

Appearance	Free flowing white powder
Specific gravity	3.35 @77°F (25°C)
Water solubility	58% (wt) @68°F (20°C)

Table 34. Characteristics of CaBr<sub>2</sub> salt

It is characterized by inhibitive properties, so this salt may reduce formation damage induced by clay dispersion and swelling.

Sodium Formate (NaCOOH) salt – is a white dry powder which is used in the mix of sodium brine, potassium/sodium formate solution. Also, may be exploited as an additive in order to enhance density of formate brines.

Potassium Formate (KCOOH) 97% salt – an organic dry salt of 97% purity. It is used to mix potassium brine, sodium/potassium solution or to increase the formate based completion brines density up to 13.1 lb/gal. This salt is a dry white powder.

The application of Potassium Formate prevents precipitations caused by the presence of calcium-based liquids in wells with high concentration of carbonate, sulphate and bicarbonate.

Advantages of application:

- 1) KCOOH is highly compatible with the formation minerals and fluids
- 2) Enhances well productivity and improves reservoir protection
- 3) Ability to be exploited in all phases of completion, avoiding costs of fluid change
- 4) Highly effective in water-sensitive formations showing excellent shale stabilization
- 5) Biodegradable, environmentally friendly and non-toxic

KCOOH can be mixed with fresh water or added to existing brine by means of rig hopper during agitating till the crystals are dissolved completely.

Physical properties:

Appearance	Free flowing white cubic crystals
pH	8.5 @73% w/w aqueous solution
Specific gravity	1.91
Water solubility	76.8% (wt) @18°C

Table 35. Properties of KCOOH

## 7.2 Fluid Loss Control and Bridging Agents

Loss of completion fluids inside permeable layers will lead to the increase of water saturation, fines migration or emulsion and scaling generation, which can significantly affect production. Also, excessive losses can complicate fluid management and well control and, as a consequence, project costs increase. Fluid loss control pills are formulated in order to control or prevent fluid invasion during and after completion operations. TETRA technologies provide following additives used in innovative completion fluids.

Linear Gel Fluids – are composed of various types of polymers in the aqueous base. Common polymers used to prepare linear gels are hydroxypropyl guar (HPG), guar, hydroxyethyl cellulose (HEC) and carboxymethyl HPG (CMHPG).

BioPol Linear Gel Pills – they are applied in order to improve economically the rheology of clear brines due to reducing the damage and invasion into the producing formations.

BioPol™ Viscosifier – high-molecular, complex polymer which is easily dispersed fine granular material used in clear-brines, fluid-loss-control pills and spacers. This type of viscosifier increases the shear rate viscosity and yield point, improving hole-cleaning and provides gel strength development.

BioPol™ L Viscosifier – high molecular weight, liquid polysaccharide polymer used in a light hydrocarbon-based oil. It is used as a primary suspending and viscosifying agent for spacers, clear brines and fluid loss control pills. BioPol L viscosifier guarantees stable rheology at temperatures higher than 120°C/250°F; overall it is an easily mixed liquid.

BioPol™ HT Viscosifier – it is a dry polymer characterized with a good compatibility with divalent clear brines and which guarantees rheology stability at the temperatures till 148°C/300°F.

TETRAVis™ Linear Gel Pills – is used in order to increase viscosities of brines applications which have less than one Darcy unit permeability. Gel polymers are easier to clean-up in formations and less damaging.

TETRAVis™ Linear Gel Pills – they are used in the single salt liquids. These gel pills are high-molecular weight hydroxyethyl cellulose (HEC) characterized by a high-purity. With oxidizing agents, enzymes and acid linear gel pills are easily degraded. For hole cleaning, fluid loss control and spacers they guarantee a broad range of viscosities.

TETRAVis™ L Linear Gel Pills – widely used in the two salts calcium bromide/chloride brine fluids. These additives are ultra-high molecular weight non-ionic HEC suspended in a hydrocarbon-free, homogeneous, environmentally safe and biodegradable mixture.

TETRAVis™ L Plus Linear Gel Pills – used in three-salt brines as the most common viscosifying polymer. These pills are liquefied HEC double-strength polymers which are exploited for the hole cleaning, fluid loss control and spacer formation. Also, it may be used as a friction-reducing agent.

### **7.2.1 Cross-Linked Pills**

In order to minimize the completion fluids loss inside the formation there are several cross-linked pills are used.

- 1) TETRAFlex™ Cross-Linked Pill – cross-linked pre-mixed gelled polymer pill which are mixed with potassium, calcium, sodium and zinc-based completion fluids in order to increase the densities.
  - a) TETRAFlex™ FLC Seal Cross-Linked Pill – applied at bottom-hole temperatures up to 120°C/250°F.
  - b) TETRA SmartSeal™ Cross-Linked Pill – it is a calcium carbonate pill used with purpose to treat from moderate to high fluid losses due to the sealing the inner screens' surfaces in the post gravel pack operations. Polymeric carrying agents, base clear brine fluid and calcium carbonate particles size distribution are individually selected for each well applications.
  - c) TETRA SmartSeal™ Pad Cross-Linked Pill – is a solids-free pill which is applied with TETRA SmartSeal cross-linked pill in order to prevent integrity and supports sealing cake's lift-off. It contains TETRA proprietary releasing agent and it is prepared on the identical base liquid and TETRA SmartSeal polymeric carrying agents.
- 2) PayZone® CleanSeal Cross-Linked Pills - it is a crosslinked polymer mixture which is used in order to control fluid losses.

The composition consists of PayZone CleanSeal XP+ and PayZone CleanSeal 10 Gel Kit which must be mixed immediately before pumping it downhole. The mixture is done easily, so there is no need for a special mixing equipment.

Typically, PayZone CleanSeal cross-linked pill is applied as a solids-free perforating pill. Above the perforation zone the gel pill is spotted and perforation guns are passing through this gel. While the well is perforated, the gel is reforming behind the guns. The gel pill is pushed across the perforated interval by the over-balance pressure following the onset of losses, so that losses are restricted almost immediately. Later the gel breaks slowly as the time passes. Break time periods are lasting from several days up to months depending on the gel formulation and reservoir temperature. However, the break time will be minimum the same days number of the stability period.

PayZone CleanSeal cross-linked pill is structured to be used in monovalent systems. It also can be applied in divalent brines. However, the pill must be designed itself based on the monovalent brines (NaCl, KCl, NaBr).

Each pill is designed for a specific case and the concentration of every component will vary.

Testing in laboratories is needed to design the pills system for individual application. In the case of a perforating pill application the gel volume essential must exceed the perforated interval volume plus volume of perforation tunnel by 50%.

From the safety point of view must be handled carefully. Ingestion and inhalation, eye and skin contacts must be avoided. In the case of skin contact must be washed by large amount of water and soap. If appropriate ventilation is not available, the properly designed respirator must be used.

#### Benefits of application:

- 1) Non-invasive and self-healing
- 2) Non-hazardous

- 3) Letting placement by means of normal rig pumps, highly shear thinning
- 4) Fluid loss control at reservoir temperature up to 248°F
- 5) Maximum obtained density is 12.5 ppg
- 6) Ability to be broken 'upon demand' or to rapidly break by means of oxidizing breakers and weak acids if it is needed.

### **7.2.2 Solids Based Pills**

Bridging and fluid loss control agents are necessary and used in TETRA fluids losses control pills as the primary agents. Across permeable intervals they provide an effective filter cake.

TETRA SmartSeal™ Solids-Based Pills – it is a carbonate pill which treats moderate to high losses of fluid by means of sealing screens internal surfaces. Polymeric carrying agents, base clear brine fluid and particle size distribution of calcium carbonate are selected individually. In order to provide high bridging efficiency, maximum liftoff at low pressures and high return permeability numbers TETRA SmartSeal pill is mixed with the TETRA SmartSeal pad.

TETRACarb™ Solids-Based Pills – CaCO<sub>3</sub> (calcium carbonate) agents are soluble in acids. They effectively seal and bridge the formations characterized by from low to medium permeability and porosity enhancing filter cake characteristics.

TETRACarb™ Pill – across the permeable intervals this agent establishes a filter cake.

PayZone® Carb Ultra Pill – it is used as a sealing and bridging agent and maintains filter cake when sand control tools are used, such as prepacked screens. Pill is removed easily by means of acidizing and is sized to flow without bridging through the prepacked screens.

PayZone® Carb Prime Pill – high-purity CaCO<sub>3</sub> (calcium carbonate) an ultra-fine-grind which is exploited as a sealing or bridging agent and mixes easily with all types of brines. The particles sizes are from lower than 1 up to 150 microns. The median (D50) size of particle is 12 microns. Carb Prime Pill seals and bridges

formations with low up to moderate permeabilities. Also, it can be exploited as an additive weight material in order to increase the fluid systems densities. Carb prime pill enhances the filtercake formation and filtration rate.

There are several benefits of PayZone® Carb Prime Pill:

- 1) Keeps particles sizes longer in comparison with the sedimentary calcium carbonates
- 2) Use in water and oil-based liquids
- 3) Removed easily by oxidizing
- 4) Designed to flow without bridging across the prepacked screens

PayZone® Carb Prime Pill must be added slowly by means of the rig hopper and well blended in order to reach uniform dispersion. The agent can be added to the circulating system directly or included in the fluid loss discrete pills.

Physical properties:

Appearance	White fine powder
pH	8.0 – 9.0
Specific gravity	2.7 – 2.9
Water solubility	0.0018 gm/100 ml H <sub>2</sub> O @100°C
Acid solubility	92% min in 15% HCL solution

Table 36. Characteristics of PayZone Carb Prime Pill

There are different concentrations based on the application purpose:

Carb Prime Pills concentration of 20 up to 60 lb/bbl is suitable to be used in pre-pack fluids. If this agent is exploited as a bridging supplement the concentration varies from 3 up to 30 lb/bbl. The concentration range of 20 to 60 lb/bbl is used in formulation of fluid loss pills.

Eye and skin contact must be avoided. Beware of ingestion and inhalation. Properly designed respirator must be provided and used in the case if the proper ventilation is not available.

TETRACarb™ Fine Pill – bridging agent select-grind to control fluid loss with particle dimensions from 1 up to 350 microns, and 55 microns value of a D50. It is also used in innovative completion fluids as a density adjustment material. The concentration applied is up to 14.0 ppg. Suitable with oil and water-based fluids and no effects on the fluids’ characteristics.

Physical properties:

Appearance	White powder
Specific gravity	From 2.7 up to 2.9
Water solubility	Minor

Table 37. Characteristics of TETRACarb Fine Pill

If it is applied as a bridging agent the concentrations of 10 – 60 lb/bbl are added. In the lightweight brines TETRACarb Fine Pills is used to enhance the densities. This additive is used only after the brine’s viscosity enhanced by adding viscosifiers of different types.

TETRACarb™ Medium Pill – a select-grind bridging agent with particle dimensions from 30 to 3350 microns and 300 microns of a D50. This bridging agent is used to control fluid losses. It is also used in high density, solids-laden and acid soluble completion fluids as a density adjustment material. The application concentration used is up to 14.0 ppg. It is characterized by high-quality materials and therefore possibility to damage the formation is low. Carb Medium pill is appropriate to use with water and oil-based fluids and does not affect their properties. The solubility in water is negligible, whereas in acids the pill is highly soluble. The usual application concentration range is from 30 up to 60 ppg. Must be added slowly through the rig hopper only after the brine was viscosified by adding of Vis L Viscosifier, Vis L HB Viscosifier or Vis HEC Viscosifier. After the pill addition all the mixture must be agitated gently to provide uniform mixing.

Physical parameters:

Appearance	White powder
Specific gravity	2.7 - 2.9
Water solubility	Low solubility in water
Acid solubility	Soluble in nitric, acetic and hydrochloric acids

Table 38. Characteristics of TETRACarb Medium Pill

TETRACarb™ Coarse Pill – this agent is characterized by D50 of 2000 microns and particles sizes from 700 up to 6000 microns.

Advantages of application:

- 1) Excellent solubility in acids
- 2) Compatible with water and oil-based fluids
- 3) Minimized formation damage due to the high-quality
- 4) Minimal effects on the fluid's properties
- 5) Highly effective in couple with the TETRA SmartSeal bridging agent

This type of pill is used in concentrations of 30-50 ppb in order to bridge across fractured or highly permeable intervals. The particle size of the CARB (approximately 30% of pills) must be one third of the pore throat dimension of formation diameter.

Before application the brine must be viscosified by means of Vis L Viscosifier, Vis HEC Viscosifier or Vis L HB Viscosifier. After the viscosity increased calcium carbonate additive must be slowly added by means of the rig hopper and to promote uniform mixing agitate gently.

Physical properties:

Appearance	White powder
Specific gravity	2.7 – 2.9
Water solubility	Negligible
Acid solubility	Solubility in hydrochloric, nitric and acetic acids

Table 39. Parameters of TETRACarb™ Coarse Pill

TETRACarb™ Flake Pill – physical sizes of this type of bridging agent is flat, rather than a conventional it is sheet like material which has spherical shape.

TETRA SS Solids Based Pills – sized salt bridging agents are made of sodium chloride's (NaCl) selected grades. By applying produced water, under-saturated sodium chloride brine or fresh water these agents can be removed easily.

TETRA SS Fine – it is characterized by particle dimensions from 1.0 up to 800 microns and 48 microns of D50 value. It is used in order to control seepage.

TETRA SS Medium Pill – is prepared from a select grind sodium chloride (NaCl) with range of particles dimensions from 100 to 1500 microns and D50 of 500 microns. This type of pill is controlling lost circulation and seepage.

TETRA SS Coarse Pill – controlling lost circulation and particles sizes range is 1000 up to 10000 microns.

### 7.2.3 Hassle-free, cost effective additives of M-I SWACO

M-I SWACO suggest fluid loss control pills which reduce losses during completion operations in openhole and cased hole and in completions after or before sand control operation.

- 1) Crosslinked and solids-free viscous pills – they are used in cased hole completions to control fluid loss by means of polymer network creation to seal the formation face or decrease losses by enhancing viscosity of fluid. It

is used before the initiation of completion that is easily removed by means of acid which clears the space for the other completion operations.

- 2) Solids-laden pills – they are applied in nonsand-control completions during perforating or to seal inside the screen after a sand control completion.

The liquid polymer fluid loss control additive material SAFE-VIS\* is a high-quality hydroxyethyl cellulose polymer (HEC) which is used in order to control losses and viscosify in seawater, freshwater or halide brine completion fluids during completion operations. There are different SAFE-VIS additives formulated to fulfill individual environmental and well requirements. They are solids-free acid-soluble and are stable up to temperature of 107°C (225°F) and depends on the base brine.

The SAFE-VIS liquid fluid loss control additives include:

SAFE-VIS E\* polymer – additive formulated in order to viscosify single-salt, CaCl<sub>2</sub> and monovalent-salt halide brines in a purified mineral oil carrier.

SAFE-VIS HDE\* high-density-brine polymer – additive designed for divalent high-density brine systems in a water-soluble carrier.

SAFE-VIS OGS\* grease- and oil-standards polymer – in a synthetic, water dispersible carrier, formulated to pass grease and oil, static sheen tests and LC50 needed for application in the environment of Gulf of Mexico. This type of pill is exploited to increase viscosity of single-salt CaBr<sub>2</sub> and CaCl<sub>2</sub>, and monovalent-salt halide brine systems.

Another type of fluid loss control additive is SAFE-LINK\* agent which guarantees control of clear brine loss inside the formation during completion operations. This type of agent is designed for specific densities comprising crosslinked chemically modified cellulose polymer. It applies highly viscous seal throughout the formation face and prevents completion fluid flow inside the formation. By application of diluted acid, the viscous material can be cleaned up easily.

This type of agent is highly effective in halide, non-zinc brines, like CaBr<sub>2</sub>, CaCl<sub>2</sub>, NaCl NaBr, seawater and KCl in density ranges from 8.6 ppg up to 15.1 ppg (1.030 kg/m<sup>3</sup> up to 1809 kg/m<sup>3</sup>). There are different SAFE-LINK agents divided by various divalent halide densities in which they are formulated:

- SAFE-LINK 110 agent – used for the brine density of nearly 11.0 ppg (1320 kg/m<sup>3</sup>)
- SAFE-LINK 135 agent – for approximate brine density of 13.5 ppg (1624 kg/m<sup>3</sup>)
- SAFE-LINK 140 agent – for the brine density of 14.0 ppg (1681 kg/m<sup>3</sup>)

Overall SAFE-LINK agent provides temperature stability till maximum 250°F and differential pressure up to 6.89 MPa (1000 psi).

SAFE-VIS OGS agent decreases by 85% the lost circulation in Gulf of Mexico.

SAFE-LINK additive is widely used in offshore Abu Dhabi and it deposits effective loss barrier in perforated and cased completions.

Solids-laden pills are used to control losses in sand control completions and provide clean perforations. The SEAL-N-PEEL fluid loss control pill is formulated to control fluid loss during completion operation inside a sand control screen. It comprises calcium carbonate particles which are sized individually for the screen openings of every application. So, it provides a fast thin tough filtercake deposition which creates an impermeable seal blocking fluid invasion across the screen.

Innovative water-based CLEANPERF WB and oil-based perforating pill CLEANPERF OB are applied with the pure systems, they are optimizing perforating operations in order to enhance productivity

In comparison with a conventional fluid loss control pills CLEANPERF WB and OB pills are designed to support pure system by laying down solids-based low-permeability barrier instantly after perforating. Easily removable robust seal is placed on the sandface, restricting effectively fluids and solids deep invasion within

and along the perforation tunnels. Created filtercake is thin and characterized by minimal cohesive and adhesive properties. Once the production is initiated the pills readily flow back without need of postcompletion remedial treatment.

The low-solids CLEANPERF OB and CLEANPERF WB pills' water phases can be designed with various base brines which include calcium bromide, calcium chloride or cesium formate in order to decrease the quantity of total solids required for density.

Another perforating operation fluid loss control system is PERF-N-PEEL which is exploited to control solids and fluids invasion while conventional perforating operations. As water-based and oil-based fluid losses pills, the PERF-N-PEEL provides a low-permeability filtercake which prevents invasion through the perforation tunnels and helps to decrease debris in the tunnel.

The PERF-N-PEEL system creates a thin seal which is removed by means of the production commencement.

Other type of fluid loss control additive is a sized-salt pill. Conventional calcium carbonate bridging solids with sized sodium chloride particles are replaced by novel sized-salt fluid loss control systems, as these bridging solids are less aggressive, water soluble breaker systems can be exploited in injector wells operations.

Sized-salt fluid loss control agents are used in different types of brines with densities higher than 10.3 ppg (1234 kg/m<sup>3</sup>). Sized-salt pills are formulated to seal the perforation tunnels sandface and in the absence of sandstones on the perforation holes where large void spaces are present. Pills are applied in order to seal perforation holes as wide as ½ in.

The sized-salt pills are removed easily by use of undersaturated injection water combination and starch-specific WELLZYME\* enzymes.

#### **7.2.4 Microfiber Bridging Agents**

TETRA Magmafiber agents are regular and fine grades are specially formulated acid soluble mineral fibers. They are coarse, long flexible materials which enhance circulation of completion fluids by means of plugging off or bridging the fractures, voids and different types of permeable formations. TETRA Magmafiber LCM (lost circulation material) is suitable for use with water and oil-based muds the same as brine-based completion fluids.

Advantages of application:

- 1) Solubility in acid
- 2) Non-fermenting and inorganic
- 3) Temperature stability
- 4) Asbestos-free
- 5) Non-polluting and non-toxic
- 6) Not corrosive
- 7) Wetted easily
- 8) Not combustible

TETRA Magmafiber is suitable to use for seepage control, plugging, bridging fractures and voids, highly effective during completion operations. This additive is compatible for innovative completion fluids, water, oil and brine-based muds, also in cement.

Treatment instructions:

The appropriate concentrations of TETRA Magmafiber is up to 30 pounds per barrel for slug treatments or like an additive material to the entire system. Normally it is used in concentrations of 0.5 bag each 30 minutes for continuous seepage to amount from 5 to 15 pounds per barrel in order to decrease seepage, total or partial losses.

When at once from 6 to 10 bags are mixed someone must be at the shale shaker to control when the pill turns to bypass or clean the shaker screen. LCM Magmafiber must be directly added in the pits and gunned or agitated inside the fluid. The

material may be blended by means of the hopper; however, this process is significantly slower. Microfibers are stable thermally above 500°F and are characterized by good compatibility with completion fluids, fresh water, and diesel oil-based brines. Also, they are exploited in order to treat lost circulation in the high bottom-hole temperatures wells.

There are different types of innovative microfiber agents:

- 1) TETRA Magmafiber Fine Microfiber Agent – it is formulated from acid soluble fine microfibers, which seal micro-fractures, under-pressured and permeable sand formations.
- 2) TETRA Magmafiber Regular Microfiber Agent – is consisted of acid soluble medium-sized materials, they are sealing under-pressured and permeable sand formations as well as micro-fractures.
- 3) PayZone 530 Microfiber Agent – composed of fine-grind acid soluble fibers usually used in fresh water and saturated salt applications. This type of microfiber is a molten spun carbonate material.
- 4) PayZone 532 Microfiber Agent - it is acid soluble coarse-grind, a molten spun carbonate microfiber, which is applied in fresh water and saturated salt uses.

Safety instructions:

Avoid eye and skin contacts, ingestion or inhalation. Properly designed respirator must be used if appropriate ventilation is not available.

### **7.2.5 pH Control and Agents**

pH levels are important in order to provide good compatibility between fluids. TETRA innovative additives are used in order to increase, decrease or stabilize pH values and to achieve the compatibility of formation fluids and brines. They also enhance the efficiency of other different additives.

There are several types of additions:

- 1) TETRA Buff-10 Agent – used in clear brines to adjust the pH level.

- 2) TETRA Buff-6 Agent
- 3) Caustic Soda

**TETRA Buff-6 Agent** - used in seawater, fresh water and clear brines to stabilize pH level. Chemically Buff-6 is an organic acid.

**TETRA Buff-10 Agent** – used in clear brine completion fluids to adjust the pH level. It is a high purity alkaline earth oxide which withstands changes of pH values up to values of 10.0 in brines or fresh water. When magnesium oxide is added to the calcium-based brine the precipitation does not occur.

Benefits of application:

- 1) Suitable to use with non-zinc halide brines, fresh water and brine polymer systems
- 2) Maintains and establishes alkalinity pH of 10 in non-zinc halide brines and fresh water
- 3) More appropriate and safer to be used to control pH level in completion fluids in comparison with caustic soda
- 4) Does not induce precipitations in magnesium and calcium brine systems

TETRA Buff-10 is added by means of chemical barrel or to the pits directly at the moment of a gentle agitation. Must not be added through a mixing hopper. The recommended concentration is from 0.1 to 0.3 lb/barrel at normal conditions.

Physical properties:

Appearance	Off-white powder
Specific gravity	2.5 -3.5 gm/cc
Water solubility	Slightly soluble

Table 40. Parameters of TETRA Buff-10

**Caustic Soda** – is a strong base (alkaline) compound which is used to maintain the sodium based clear brine fluids' alkalinity. Another name of caustic soda is a sodium hydroxide. It is added by means of chemical barrel or at a point gentle agitation directly to the pits. It is not added through a mixing hopper.

Physical properties:

Appearance	Odorless, white solid
pH	13 @1% (M) aqueous solution
Specific gravity	2.13 @68°F (20°C)
Water solubility	Soluble

Table 41. Characteristics of caustic soda

Benefits of application:

- 1) Efficient at small treatment levels
- 2) In the most tubular goods the reduced corrosion rates are shown
- 3) Not suitable to use in the divalent brines
- 4) Source of hydroxyl ions in order to control pH, highly economical

Formation water, fluid additives and contacting fluids must be screened for compatibility with the brines.

### **7.3 Additives used in completion fluids for formation protection**

There are different types of additives used in order to protect or minimize the formation from damage. These products include:

- 1) Iron control agents
- 2) Non-emulsifiers
- 3) Scale Inhibitors
- 4) Clay stabilizers

Safety problems:

Good ventilation must be provided at the work place. Sparks, hot surfaces, heat, open flames and ignition sources may cause a danger. Personal protective equipment must be used. Skin and eyes contact must be avoided, do not breathe the gas, mist, dust, fume, vapors, spray. The contaminated clothes must be washed before reuse. The product must be handled carefully.

Iron Control Products – formation damage can be induced by the iron compounds precipitation. As a consequence, decrease of reservoir permeability or exacerbate

sludging issues. There are two classes of iron control agents: chelates and reducing agents.

FerroBan™ Iron Control Agent is an organic iron sequestrant and reducer which is used in divalent or monovalent completion fluids. After application of this agent the ferric iron reduces to the ferrous iron which is more preferable and is characterized by excellent stability and solubility in different types of fluids and at a wide range of pH values. Also, by chelation the FerroBan agent maintains iron in the solution. So, it preserves from sulfide and iron hydroxide precipitation.

Advantages of FerroBan™ Iron Control Agent:

- Dissolved easily in brines
- Highly compatible and soluble in seawater, potassium, calcium, zinc and sodium brine systems
- Effective and fast acting at the low temperatures

Application instructions:

FerroBan iron control agent must be added at the suction side of the pump into the completion fluid just prior to pumping the fluid downhole. Aeration of the liquid during the Ferroban agent addition must be avoided. The disadvantage is that the agent is incompatible with different metals, acids, bases and various types of oxidizing materials. Must be handled carefully, skin and eye contacts, also ingestion and inhalation must be avoided. If proper ventilation is not provided, the adequately designed respirator must be used.

The concentration of iron control agent depends both on the total concentration of iron and the ferric iron amount.

The treatment recommended rates for this type of agent changes from 20 up to 105 pounds per 100 barrels of liquid relying on the iron concentrations. Additionally, there are various factors which must be take into account when the optimum rate of treatment for the iron control agent must be selected.

Physical properties:

Appearance	White odorless powder
Incompatibilities	Metals, acids, bases, oxidizing materials
Flash point	N/A
pH	5.5 – 8.0
Specific gravity	1.20
Viscosity	N/A
Water solubility	Soluble

Table 42. Properties of FerroBan iron control agent

Non-Emulsifiers – in the formation the residual oil in contact with the water-based brines can generate emulsions during fracturing and other stimulation treatments or after them. Non-emulsification agent breaks in-situ an emulsion prior to the simulated well is set on production. These agents prevent emulsions to occur downhole and to clog the wellbore. As a consequence, by preventing the wellbore productivity of oil and gas reaches maximum value and improved production after cleanup.

PayZone® NE 200 Non-Emulsifier – an emulsion preventer agent which is used with calcium-based completion fluids and inhibits emulsion formation induced by the hydrocarbons and completion brines mixture. Emulsions cause the formation damage and consequently hinder the ability of formation to let the fluids pass. The recommended concentration range must be added to the brine is approximately from 1.5% to 2% by volume.

Benefits of application:

- Suitable to be used in gas and oil producing formations
- Preventing oil-brine emulsions formation, miscible in the calcium brine systems
- Maximizes the completion fluid recovery by reducing the brine surface tension
- The effective low concentrations are from 0.1% up to 1.0% by volume

Physical properties:

Appearance	From clear to amber fluid
Specific gravity	0.84 – 0.87
Water solubility	Dispersible

Table 43. Characteristics of PayZone® NE 200 Non-Emulsifier

PayZone® NE 300 Non-Emulsifier – it is applied to the zinc-based completion fluids as an emulsion preventer, because when hydrocarbons mix with the completion brines emulsions may form and induce the formation damage.

Advantages of application:

- Used in gas and oil producing reservoirs
- Compatible with the zinc-based brines, hindering oil-brine emulsions formation
- Non-emulsifier Payzone NE 300 is added and mixed easily with the active systems
- Decreases surface tension of brines and consequently completion fluid recovery enhances
- The effective low concentrations are between 0.1 and 1.0% by volume
- Recommended treatment non-emulsifier concentrations are from 0.1% up to 1.0% by volume

PayZone NE 300 is easily mixed with zinc brines and is applied before the fluid introduction inside the wellbore. This agent can be used together in a clear brine together with a mutual solvent.

Physical properties:

Appearance	From clear to amber fluid
Density	0.84 – 0.87 g/cc @20°C
Water solubility	Soluble

Table 44. Parameters of PayZone® NE 300 Non-Emulsifier

PayZone® NE 400 Non-Emulsifier – it is exploited to use for calcium-based completion fluids as a high-performance non-emulsifier material.

Advantages of application:

- Compatible and soluble in the calcium-based completion fluids
- Guarantees clean fast oil/brine emulsion brine and prevents emulsion formation by means of pre-treatment
- NE 400 agent easily mixes with the active system
- Decreases brine surface tension and enhances the recovery of the completion fluid
- Application of low concentrations are effective from 0.1% up to 1.0% by the volume
- Not compatible to use with monovalent and zinc-based brine systems

NE 400 non-emulsifier is mixed with calcium-based fluids and is added before sending fluid inside the wellbore. It is added before the exposure to reservoir fluids in order to inhibit the oil/brine emulsions formation caused by of two fluids contact. The recommended treatment concentration is between 0.1% and 1.0% by volume to the brine.

Physical properties:

Appearance	From clear to light yellow color liquid
Specific gravity	0.965 – 0.972
Water solubility	Soluble at temperature 25°C

Table 45. Properties of NE 400 non-emulsifier

PayZone® NE-500 non-emulsifiers – highly effective additive used in the CaCl<sub>2</sub> based and divalent completion fluids. It is effective at one-fifth of the required treatment of different non-emulsifier products and shows perfect performance at the breaking of brine/oil emulsions.

### Benefits of application:

- Consistent with all divalent brines (involving zinc-based and CS Neptune completion fluids)
- Effective in brine/oil emulsion breaking (particularly with CaCl<sub>2</sub> brine systems and divalent completion fluids) among the different oil/brine and crude oils ratio
- In comparison with other non-emulsifier agents it shows the same or better performance requiring substantially less products
- Reduced safety concerns because there is no isopropyl alcohol used in its formulation

### Physical properties:

Appearance	Clear, pale amber solution
Odor	Slight solvent
Specific gravity	0.988 g/mL
Water solubility	Soluble

Table 46. Parameters of PayZone® NE-500 non-emulsifiers

NE-500 non-emulsifier is applied for both divalent completion fluids and CaCl<sub>2</sub>-based brine systems breaking any brine/oil emulsions which may form during the well life cycle. The recommended concentration used is 0.1% by volume.

PayZone® NE 600 – highly effective non-emulsifier mostly used in monovalent completion fluids as CS Neptune fluids and standard halide brines. It breaks oil/brine emulsions.

### Advantages of application:

- Used with all types of divalent completion fluids which include TETRA CS Neptune and zinc-based brines
- Formulated without isopropyl alcohol and therefore less risky from safety point of view

- Across oil/brine and multiple crude oil ratios this agent provides emulsion breakup
- Highly effective in use with standard halide brines, monovalent and CS Neptune completion fluids
- Mostly used in zinc-base brine systems during the well life cycle

Physical properties:

Appearance	Amber clear mixture
Odor	Slight solvent
Specific gravity	1.085 g/mL
Water solubility	Soluble

Table 47. Parameters of PayZone® NE 600

PayZone® NE 700 – non-emulsifier additive highly effective in the zinc-based brine systems. It shows a good performance of breaking up the brine/oil emulsions formations. The recommended concentration to use is 0.1% by the volume.

The benefits of application:

- Used in divalent completion fluids, including TETRA CS Neptune and zinc-based brine systems
- Effective in CaBr<sub>2</sub> and ZnBr<sub>2</sub> brine systems, this additive provides emulsion effective breakup across oil/brine and multiple crude oil ratios
- In comparison with the other non-emulsifiers NE-700 additive requires less products in order to achieve better or the same performance
- Less safety concerns because it does not include isopropyl alcohol

Physical properties:

Appearance	From colorless to pale amber clear mixture
Odor	Slight solution
Specific gravity	0.965 g/mL
Water solubility	Soluble

Table 48. Properties of PayZone® NE 700

### **7.3.1 Scale inhibitors**

Another additive which is used in innovative completion fluids are scale inhibitors. Most of industrial waters contain alkaline metal cations as magnesium, calcium and different anions as carbonate, bicarbonate, oxalate, sulfate, silicate, phosphate and fluoride.

Anions and cations combinations present in concentrations exceeding their reaction products solubility may precipitate until the product solubility concentrations are no more exceeded. Precipitated products are alkaline earth metal scales. When calcium ion concentrations and ion of carbonate exceed calcium carbonate product of reaction solubility, consequently a calcium carbonate scale's solid phase will be formed as a precipitate.

Compositions of scale inhibitors together with the polymeric structures are characterized and described by having a carboxylic acid group and a sulfonic acid, in addition to a phosphonomethylamino group. By including into a single molecule, the several types of functional groups, control of scale deposition and formation under severe conditions than normally encountered can be achieved.

PayZone® SI 139 Scale Inhibitor – inhibits calcium sulfate, calcium carbonate and barium scales in the light-density completion fluids. This type of scale inhibitor is a triphosphonic acid which is based on the adenosine monophosphoric (AMP). It is characterized by temperature-stability up to 176°C/350°F.

### **7.3.2 Innovative Clay Stabilizers used in completion fluids**

Reactive clays presence may cause dispersion, swelling and migration which can negatively affect the results of production. Therefore, these additives are used in the completion fluids in order to prevent these problems.

PayZone® Clay Stay Clay Stabilizer – the most commonly used clay-stabilizing additive which is compatible with all types of completion fluids. This additive prevents and stabilizes the swelling and hydration in interstitial clay.

PayZone® StrataFix Clay Stabilizer – is a combination lubricant and shale inhibitor for water base systems. PayZone StrataFix is an additive suitable to use with the clear brine fluids and prevents dispersion and adsorption of water in water sensitive shales. When combined with a brine fluid will generate synergistic effect and enhance shale stability and will decrease the possibility of differential sticking.

### **7.3.3 Hydrate Inhibition**

When water mixes with natural gas the gas hydrates start to form which are an ice-like white crystallines. They are insoluble in the fluid itself. It forms at conditions of low temperatures and high pressures. Gas molecule also known as a Clathrate Hydrate is held in a cage which is formed by water molecules. There are special inhibitors used in completion fluids to control hydrates formation. The lower-boiling or smaller hydrocarbon molecules especially from methane to C4 hydrocarbons and mixtures are characterized by easier crystals formation.

For ethane hydrates form at pressure about 1 MPa and temperature of 4°C. For ethane the pressure is 3 MPa and temperature of 14°C. Also, non-hydrocarbons as nitrogen, hydrogen sulfide and carbon dioxide are forming hydrates at certain conditions. There are 2 different techniques in order to control or overcome the hydrate formation:

- 1) Thermodynamic
- 2) Kinetic

Thermodynamic approach includes water removal, temperature increasing, pressure decreasing, adding of antifreeze to the fluid.

Kinetic method controls formation of hydrates by using various materials named inhibitors. Onium additives with four carbon substituents are added to prevent conduits plugging by formation of gas hydrates. Also, polymers characterized by presence of the lactam rings are exploited as clathrate hydrates inhibitor used in the completion fluid systems.

## 8. Conclusion

Application of solids-laden fluids can worsen the production of reservoir and damage downhole completion equipment. For this reason, clear-brine completion brines are preferred to be used as an alternative. Clear brines are made of formate or halide salts dissolved in water. However, they also have drawbacks, as the salts contained in these fluids at increased pressures or lower temperatures can crystallize inducing potential costly operational disruptions and well control issues.

Cesium formate brines may restrict supply and cause higher costs in high-volume deepwater applications induced by the brines limited production. Moreover, formates may lead to the hydrogen-induced cracking (HIC) typically in the carbon dioxide (CO<sub>2</sub>) presence and cause the failure of production tubing.

Zinc-based fluids are priority pollutants causing harmful effects on the environment and increasing potential of metal components corrosion due to the low pH value (acidity), therefore causing personnel safety.

Therefore, taking into account all drawbacks of conventional completion fluids, innovative priority-pollutant-free and high-density fluids were developed.

The result of lab-scale testing and development showed that the innovative high-density non-zinc (HDNZ) solids-free completion fluid met all requirements and challenges related to ultra-deep-water environments for fluid densities ranges from 14.5 lb/gal up to 15.4 lb/gal. This type of system showed major improvement of performance in comparison with formate and aqueous halide completion fluids.

Application of the novel HDNZ system at real field conditions confirmed the results of performance at the lab-scale testing. So, the system showed excellent stability and robusticity and therefore it became a real viable alternative to the conventional completion fluids.

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