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Subject	: Diesel blanket alternatives

Introduction

Blanket fluids are used in salt solution mining caverns to control the shape of the cavern, slow down the vertical dissolution and stabilize the cavern roof. Blanket fluids are inert to the salt and are less dense than the injected water and consequently the brine. The blanket fluid is pumped in the cavern, as a result a distinguishable separate layer exists on top of the brine filled cavern volume.

The blanket fluid commonly used in the salt solution mining industry is diesel. This is because diesel has good physical properties to act as an inert blanket fluid. Nedmag has used red diesel (EN590 10 ppm B0, denoting a content of 10 ppm sulphur and 0% biodiesel) in the past 40 years, showing good stability. However, diesel's toxicity to humans and the environment as well as flammability makes diesel less suited from an HSE point of view. Therefore, this memo investigates potential blanket medium alternatives.

Discussion

In order for a chemical to act as a blanket fluid, it needs to meet certain criteria. The below listed criteria are all important when comparing blanket fluid alternatives to diesel. The criteria are:

1. HSE:

   General requirements with respect to toxicity to humans, environment and aquatic organisms must be as low as possible. Also, the use of gases as a blanket medium will increase the surface annulus and wellhead pressure, causing an increased risk during operations.

2. Density:

   The density of the blanket fluid is required to be lower than that of the injected water and cavern brine to ensure that the blanket fluid is more buoyant and will support and protect the cavern roof.

3. Solubility:

   The solubility of blanket fluid in brine needs to be as low as possible, as any solubility will cause the blanket and cavern fluid to mix. This will also result in loss of injected blanket fluid into the cavern which will eventually reach the production stream. The solubility of salts in blanket fluid also needs to be minimal, in order to prevent unwanted leaching processes. Miscibility will also cause the interface to disperse which will make the density log interface depth interpretation more difficult.

4. Measurability:

   To maintain control over the fluid blanket and cavern growth, it is necessary to determine the exact position of the blanket fluid brine interface. This is performed by neutron-density logs which therefore need to be able to distinguish between cavern brine and the blanket fluid to determine the blanket depth. Also, pressure measurements of the blanket fluid allow pressure gradient calculations to predict blanket fluid interface depth.

5. Freezing, boiling and flash temperature

   The temperature dependent physical state of the fluid must be such that it will remain liquid within the range of the working temperature on surface and within the cavern. For the chemical to be handled safely the flash temperature, the temperature under which the chemical can ignite when given an ignition source, preferably must be similar or higher than that of diesel (~50 °C).

6. Stability:

   Lack of chemical stability, either by deterioration under high temperature, pressures or by microbial decomposition will cause a loss of effective blanket fluid. Microbial deterioration can increase HSE risks as it can cause methane production, slug forming, as well as corrosion to steel equipment. As injected water is a continuous source of microbes, bioactivity could accumulate in susceptible fluids. The stability of a blanket fluid could also be influenced if the fluid easily permeates through the surrounding cavern salt.

7. Handling:

   Easy handling will result in reduced injection and operational time. One example is the viscosity of the blanket fluid, which will need to be low enough such that it can be pumped readily. On the other hand, the use of gases will increase handling difficulty as it will need special high-pressure equipment to store, compress and monitor flow.

8. Price:

   Because the volume of blanket fluid needed to support a cavern are very large (2500 m^3 diesel per cavern is expected for VE-5 and VE-6 during cavern growth) the price is important for salt solution mining (unit price of diesel is approximately € 0,36/ltr, as per diesel budgeting Nedmag June 2017).

Group of chemicals evaluated

In total 7 different groups of chemicals have been evaluated on the previously described criteria. HSE of chemicals is expressed using the NFPA 704 ((H)ealth, (F)ire, (R)eactivity) rating system denoted on the safety data sheets of a specific substance. Here the degree of hazard is denoted using numerals (0, 1, 2, 3, 4) indicating low (0) to high (4) H, F and R hazards.

Gases

Gases are inert to salt and, therefore, a gas blanket could be used to protect the cavern roof from dissolution into the injected water. Gases have densities three order of magnitude lower than that of most liquids under standard conditions, this low density reduces the head exerted on the cavern liquid resulting in high casing and wellhead pressures. Petroleum gas is highly flammable inducing large fire and explosion risks. Nitrogen is a widely available, low reactive and low toxic gas

Assuming a mid-cavern depth of 1900 m TVD (planned depth of VE-6 well), using the average lithostatic specific gravity of 2.31 results in a maximum cavern pressure of 431 bar. Nitrogen at 95 °C and 431 bar is compressed to 0.31 kg/m^3, generalizing this density over the entire annular well volume (overestimating the gas' exerted head) would result in a WHP of at least 373 bar. This induced the need of 10K pressure rated wellheads and gas sealing equipment, increasing capital investment substantially. Current casing designs would meet the pressure rating as the internal yield of 9 5/8" 47# L80 and collapse resistance of the 7" 29# L80 (design blanket casing annulus of VE-6 below the wellhead) of 430 and 440 bar (considering a safety factor of 1.1), respectively, would not be reached. However, because gases are highly compressible, the compressibility of nitrogen at 431 bar at 95 °C is approximately 306 m^3/m^3. This compressibility introduces a large HSE risk as loss of well control or integrity would result in explosive expansion of 765.000 m^3 (2.500 m^3 x 306) of nitrogen gas. In addition, highly compressed gas can become trapped under the cavern roof during cavern development, which introduces the risk of sudden release of high pressure gas pockets into the well.

Due to the small molecular size of nitrogen it can more easily permeate through the surrounding salt in caverns[1], therefore the use of nitrogen would require constant monitoring and injection to maintain the desired blanket pressure. Nitrogen cost are relatively low (0,43 €/Nm^3 quote WSG 2016), taking compressibility into account this equates to approximately 0.13 €/ltr. However, handling of gas will require specialized high-pressure equipment to store, compressor and monitor gas flow.

The benefit of nitrogen's low toxicity is not seen to counterbalance the large HSE risks and other disadvantages associated with working with highly compressed gases as a cavern blanket medium alternative.

Table 1 Properties of gases

Chemical	HSE	Specific gravity	Solubility in water	Flash point	Boiling point	Freezing temperature
	H, F, R	-	mg / l	°C	°C	°C
Diesel	**1,2,0**	**0,813**	**16 - 45**	**70**	**170 - 390**	**-18 - -8**
Gases						
Nitrogen	0,0,0	0,0013	20	-	-196	-210
Butane	1,4,0	0,0025	61	-60	-1 - 1	-140 - -134

Esters

Esters are a group of chemicals derived from the esterification of an alcohol and carboxylic acid. Generally, esters are highly flammable (indicated by their low flash point temperature) and miscible in water, both of which reduce with the increasing length of the organic chain length as shown in Table 2.

Pure biodiesels are chemically produced fatty acid methyl esters (FAME), typically made by transesterification of organic chain fatty acids (obtained from a vegetable or animal source) with methanol. They have a density lower than water, low solubility in water and relatively high boiling- and flash point. Although the physical properties are similar to that of diesel, because biodiesel is chemically produced it does not hold sulfide containing compounds and aromatics that are found in petroleum diesel. This makes biodiesel less toxic and more environmentally friendly. Current diesel fuels are mixed up to 7 % biodiesel named diesel B7. Due to the polar chemical structure, biodiesel is more hygroscopic (attracting water from the environment) than petroleum diesel. Growth in microbial activity, both aerobe and anaerobe, in biodiesel in contact with water has been widely reported in studies[2]. The possible growth of methanogens in biodiesel, and even in biodiesel blends with fossil diesel, could potentially cause a partial conversion of biodiesel to methane inflicting a high risk of fire and explosion hazards. To add to this, microbial growth can also incur corrosion to metal equipment[3,4].

Fuel supplier AVIA has stated that the use of biodiesel could lead to sludge development due to its interaction with water and oxygen, a process that could continue when pumped into the well until oxygen is depleted. Also, corrosion was known to affect storage tanks, even with diesel/biodiesel blends. However, biodegradation under anaerobic cavern conditions is unknown, and is hence still a significant risk preventing it's application. The addition of biocides could be used to attempt to reduce biodegradation[5], however its subsurface effectiveness will most likely reduce over time and the use of biocides introduce unwanted HSE risks.

Because biodiesel is synthetically produced their unit price is 60% higher (~€0.60/ltr, assuming fuel taxes are not applicable) than that of diesel.

Table 2 Properties of esters

Chemical	HSE	Specific gravity	Solubility in water	Flash point	Boiling point	Freezing temperature
	H, F, R	-	mg / l	°C	°C	°C
Diesel	**1,2,0**	**0,813**	**16 - 45**	**70**	**170 - 390**	**-18 - -8**
Esters						
Methyl methanoate	2,4,0	0,98	miscible	-19	32	-100
Methyl ethanote	1,3,0	0,98	250000	-10	56,9	-98
Methyl propanoate	2,3,0	0,915	72000	-2	80	-88
Propyl propanoate	4,2,0	0,833	2745	19	123	-76
Pure biodiesel	0,1,0	0,88	13 - 100	100 - 170	315 - 350	-5 - -10

Renewable diesel

Similar to biodiesel, renewable diesels have been developed to lower CO_2 emissions from combustion engines. Hydrogenated vegetable oil (HVO), is produced via a process where waste and residue fat fractions are used to produce renewable diesel by hydrotreating and isomerization. Renewable diesels are made of hydrocarbons similar to existing diesel fuel components with virtually no toxic components (very low content of aromatics and Sulphur), resulting in similar physical properties to that of diesel but with a lower flash point. Because of the different production process to that of biodiesel, renewable diesel does not have a polar chemical structure and therefore does not attract water like biodiesel. The safety data sheet of HVO states its potential to biodegrade. Price of a renewable diesel is 2-3 times higher than diesel, ~€1.10/ltr assuming fuel taxes are not applicable.

Table 3 Properties of renewable diesels

Chemical	HSE	Specific gravity	Solubility in water	Flash point	Boiling point	Freezing temperature
	H, F, R	-	mg / l	°C	°C	°C
Diesel	**1,2,0**	**0,813**	**16 - 45**	**70**	**170 - 390**	**-18 - -8**
Renewable diesel						
HVO	0,2,0	0,77 - 0,79	Low misciblity	61	180 - 320	-20

Insoluble fatty acids

Insoluble fatty acids are the main constituent of vegetable oils. Table 4 shows a list of the most common vegetable oils. Vegetable oils have low toxic effects to human and environment. Also, their high flash point results in low flammability. Vegetable oil's density is lower than that of water and can be handled in a wide temperature range, although some oils have high freezing temperatures, making handling in cold water difficult. The smoking points of oils, the temperature at which visible smoke and potential carcinogens are generated, are high and above working temperatures. By definition they are insoluble in aqueous liquids. Microbial growth under cavern conditions is unknown. Vegetable oils are reported to be biodegradable under both aerobic and anaerobic conditions, also 70 – 100 % biodegradation is reported in a period of 28 days[6]. The potential biodegradation can cause deterioration of the blanket fluid as well as HSE risks and corrosion hazards. The price of vegetable oils per liter vary greatly (approximately 2 - 10 times that of diesel).

Vegetable oil supplier LEVO supported the fact that insoluble fatty acids are quickly deteriorating in direct contact with light and oxygen, by oxidative degeneration. However, no statement could be made about its stability under cavern conditions over extended periods.

Table 4 Properties of insoluble fatty acids

Chemical	HSE	Specific gravity	Solubility in water	Flash point	Boiling point	Freezing temperature
	H, F, R	-	mg / l	°C	°C	°C
Diesel	**1,2,0**	**0,813**	**16 - 45**	**70**	**170 - 390**	**-18 - -8**
Insoluble fatty acids					Smoke points	
Castor Oil	1,1,0	0.960-0.96	Low miscibility	229	-	-10
Coconut Oil	-	0,926	Low miscibility	295	177	21.2-25.2
Corn (Maize) Oil	0,1,0	0,921-0,928	Low miscibility	325	230	-11
Linseed Oil	0,1,0	0,930-0,938	Low miscibility	222	-	-19
Olive Oil	0,1,0	0,915-0,920	Low miscibility	242	190	-6
Palm Oil	0,1,0	0,924	Low miscibility	324	-	35
Peanut Oil	0,1,0	0,917-0,926	Low miscibility	334	225	3
Soybean Oil	0,1,0	0,924-0,927	Low miscibility	330	257	-16
Sunflower Oil	0,1,0	0,925	Low miscibility	319	225	-17
Rapeseed Oil	0,1,0	0,910 - 0,923	Low miscibility	326	236	-10

Refined petroleum products

Potential petroleum refined alternatives similar to diesel are Surdyne B140, Exxsol D100 and GTL. Surdyne B140 is used as a base oil for oil-based mud (OBM) during drilling operations. Surdyne B140 is refined by hydrogen treatment in order to lower sulfur and aromatics content making it lower in toxicity to human and the environment. The safety data of Surdyne B140 states no carcinogenicity, and no toxicity to aquatic life or other living organisms. Also, transport is more practical as it is not classified as dangerous good under ADR regulations. The measurability of chemicals is proportional to the proton density, as the chemical formula is not known, estimation of the measurability is uncertain. However, as it is a petroleum derivative its measurability by neutron-density tools will be in the same order of magnitude as diesel. The safety data sheet denotes the potential of Surdyne B140 to biodegrade, it is unknown if under cavern conditions this could incur large HSE risks preventing its application. The price of Surdyne B140 varies with the oil price, a quotation from Chemfor January 2017 stated €0.64 per liter (approximately 2x price of diesel).

Drilling fluid specialist of MI-SWACO stated no issues with prolonged storage of Surdyne B140, they have not encountered methane production in OBM (Surdyne B140 as base oil) containing abandoned wells.

Exxsol D100 is produced from petroleum-based raw materials which are treated with hydrogen in the presence of a catalyst to produce a low odor, low aromatic hydrocarbon solvent with a high flash point. Similar to Surdyne B140, this refined petroleum based solvent has lower toxicity to humans and aquatic organisms compared to diesel. Similar as for Surdyne B140, the safety data sheet of Exxsol D100 states the potential to biodegrade, although it is unknown if under cavern conditions this could incur large HSE risks, preventing its application. Brenntag has quoted Exxsol D100 at €0.63 per liter (approximately 2x price of diesel). Initial feedback from Brenntag stated no issues with prolonged storage, however, additional feedback on potential stability downhole could not be made.

Gas to liquid (GTL) is an alternative fuel to diesel made from natural gas by means of Fischer Tropsch, Mobil or syngas to gasoline plus processes, and therefore nearly free of aromatics and Sulphur components known to be found in petroleum diesel. The flashpoint of GTL is lower than that of diesel increasing its flammability. The safety data sheet states the potential to biodegrade. The price of GTL is approximately 1.14 times (~€0.41/ltr, assuming Oliecentrale fuel price listing 2017 and that fuel taxes are not applicable) the price of diesel. To our knowledge GTL has not been used for downhole applications.

Although the material safety data sheets of Surdyne B140, Exxsol D100, GTL or HVO state that they are biodegradable, the contents of these chemicals are similar to the main components of diesel (saturated hydrocarbons). Therefore, when considering the hazard if blanket medium leaks off into fresh water formations these alternatives would have a long exposure timescale before it is fully degraded, depending on environment (oxygen concentration, water salinity and temperature). To be able to use a refined petroleum product it needs to undergo long-term testing under downhole conditions to identify if the product is subjected to microbial deterioration.

Table 5 Properties of refined petroleum products

Chemical	HSE	Specific gravity	Solubility in water	Flash point	Boiling point	Freezing temperature
	H, F, R	-	mg / l	°C	°C	°C
Diesel	**1,2,0**	**0,813**	**16 - 45**	**70**	**170 - 390**	**-18 - -8**
Petroleum refined						
Surdyne B140	0,1,0	0,796	Low misciblity	95	220 - 275	-30
Exxsol D100	0,1,0	0,817	Low misciblity	100	240 - 267	-75
GTL	1,2,0	0,765 - 0,8	Low misciblity	60	176 - 370	n/a

Glycols

Glycols are higher order alcohols and are, like low molecular weight alcohols, miscible in water. Glycols are a group of chemicals that are generally less toxic to humans and the environment. Glycols are generally less flammable than diesel and have a density higher than that of fresh water. Glycols are fully miscible in fresh water, also a major drawback is the known high solubility of $MgCl_2$ in ethylene glycol. Reported solubility of $MgCl_2$ in ethylene glycol is 10 to 20 % (w/w)[7]. The above stated makes glycols an unsuited alternative to diesel as a fluid blanket. As glycols are chemically produced from refined organic compounds their unit price is approximately 3 - 7 times (€1.00-€2.50/ltr) that of diesel.

Table 6 Properties of glycols

Chemical	HSE	Specific gravity	Solubility in water	Flash point	Boiling point	Freezing temperature
	H, F, R	-	mg / l	°C	°C	°C
Diesel	**1,2,0**	**0,813**	**16 - 45**	**70**	**170 - 390**	**-18 - -8**
Glycols						
Mono Ethylene Glycol	1,1,0	1,114	miscible	118	198	-12,9
Tri-Ethylene Glycol	1,1,0	1,124	miscible	116	288	-7
Propylene Glycol	0,1,0	1,053	miscible	>100	214	-59
Hexylene Glycol	2,2,0	0,922	miscible	93	198	-40

Ethers

Ethers are compounds containing generally two organic groups that are bound to one oxygen atom. Although the toxicity and reactivity of ethers are generally low. The physical properties of ethers depend on the complexity and size of the organic groups. Generally, the boiling, flash and freezing temperatures increase with the increasing size. However, the flash points of ethers are very low making them highly flammable. The solubility of ether in water depends on the type of ether. As can be seen in Table 7, the solubility of the denoted ethers ranges from fully miscible to 3 g per liter of water. Ethers are chemically produced from refined organic compounds; therefore their unit price is higher than that of diesel approximately 4 – 7 times (€1.40-€2.50/ltr) that of diesel.

Table 7 Properties of ethers

Chemical	HSE	Specific gravity	Solubility in water	Flash point	Boiling point	Freezing temperature
	H, F, R	-	mg / l	°C	°C	°C
Diesel	**1,2,0**	**0,813**	**16 - 45**	**70**	**170 - 390**	**-18 - -8**
Ethers						
Methoxyethane	2,2,0	0,725	miscible	-41	7,4	-113
Methoxypropane	2,3,0	0,736	30500	-20	38,8	-
Di-ethyl ether	1,4,1	0,713	6050	-45	34,6	-116,3
Propoxypropane	2,3,0	0,75	3000	-18	90	-122

Alcohols

Alcohols are organic compounds with a hydroxyl group (-OH) bound to a carbon atom. They can be produced biologically, such as methanol and ethanol, or synthetically like most larger and complex alcohols. The alcohol functional group (-OH) can form hydrogen bonds with water, therefore most alcohols are fully miscible in water. The toxicity of alcohols to humans and environment differs. While methanol and ethanol are toxic to humans, it is found to be of low toxicity to aquatic organisms. Most low molecular weight alcohols have low flash point temperatures making them highly flammable. The solubility reduces with the increase of molecular weight, or size of the organic molecule. The solubility of long chain alcohols, like n-decanol is still around 3.7 g per liter of water. The increasing molecular weight of n-decanol causes the freezing point to increase to 6 ˚C which would make handling in cold weather difficult. Because of these reasons alcohols are not suitable as an alternative to diesel as a blanket fluid. The unit price of alcohols is generally higher than that of diesel (2 – 6 times that of diesel, €0.70-€2.20/ltr).

Table 8 Properties of linear alcohols

Chemical	HSE	Specific gravity	Solubility in water	Flash point	Boiling point	Freezing temperature
	H, F, R	-	mg / l	°C	°C	°C
Diesel	**1,2,0**	**0,813**	**16 - 45**	**70**	**170 - 390**	**-18 - -8**
Alchols						
n-Methanol	1,3,0	0,792	miscible	12	64,7	-97,6
n-Ethanol	2,3,0	0,789	miscible	17	78,2	-114,1
n-Propanol	1,3,0	0,803	miscible	22	98	-126
n-Butanol	1,3,0	0,81	73000	35	117,7	-89,8
n-Pentanol	2,3,0	0,811	45000	49	138	-78
n-Decanol	2,2,0	0,83	3700	108	232,9	6,4

Conclusions and recommendations

Table 9 shows a qualitative visualization of the chemical groups' criteria evaluation. From the evaluated chemical groups, biodiesel, refined petroleum products like Surdyne B140, Exxsol D100 and GTL, renewable diesel and vegetable oils have similar physical properties to that of petroleum diesel to function as a blanket fluid in salt caverns, while being lower in toxicity. A potential issue with oil substances with lower toxicity is biodegradation. Anaerobic microbial growth in the blanket fluid could incur large HSE risks both due to the potential conversion to methane, sludge formation and microbial induced corrosion of steel equipment.

Biodiesels have hygroscopic properties due to their molecular structure. Stated by a supplier of biodiesel, the attraction of water in presence with oxygen is known to form sludges by biodegradation. This process would continue inside the well until all oxygen is depleted. In addition, corrosion to storage tanks is reported, which could damage the integrity of the blanket casing.

Literature has shown that vegetable oils are fully degradable both aerobic and anaerobically. Suppliers could not comment on stability in a salt solution well, however, it was stated to readily degrade under exposure of oxygen.

Petroleum refined products like Surdyne B140, Exxsol D100 and GTL as well as renewable diesel all have similar hydrocarbon components compared to diesel but with virtually no aromatic content and Sulphur containing compounds. Price of some of these products is 2 times more expensive than diesel. GTL and HVO have a lower flash point compared to diesel, increasing their flammability. SurdyneB140 and Exxsol D100 are potential alternatives with a higher flash point and lower toxicity, reducing the health and fire risks compared to diesel. Suppliers have not experienced issues regarding degradation during storage for longer periods. Surdyne B140 is a common base oil used as drilling fluid, and the supplier stated no stability issues on surface and in wells.

Although the material safety data sheets of Surdyne B140, Exxsol D100, GTL or HVO state that they are biodegradable, the content of these chemicals are similar to the main components of diesel (saturated hydrocarbons). Therefore, when considering the hazard if blanket medium leaks off into fresh water formations these alternatives would have a similar long exposure timescale before it is fully degraded, depending on the environment (oxygen concentration, water salinity and temperature).

As stated above biodegradation in the possible alternatives under cavern conditions is unknown. Assuming that temperature and water salinity have a higher influence on biodegradation than pressure, samples of petroleum refined products, Surdyne B140 or Exxsol D100, and its blends with diesel can be tested for potential biodegradation. The products need to undergo long-term testing under downhole conditions to identify if the product is affected by microbial deterioration.

Table 9 Criteria visualization (criteria are denoted +/++ if the chemical has desired properties and -/-- if undesirable. * denotes the assumed measurability when molecular formula is unknown, ** denotes estimations obtained from figures on internet)

	HSE (H, F, R)	Density	Solubility	Measurablilty	Freezing, boiling and flash temperature	Stability	Handling	Unit price
Diesel	-	++	++	++	+	++	++	++
Gases								
Nitrogen	++	++	++	++	++	--	--	++
Petroleum gas	--	++	++	++	--	--	--	**-
Esters								
Short organic chain esters	--	++	--	++	--	-	-	**--
Biodiesel	+	++	++	*++	++	-	++	**-
Renewable diesels								
HVO	+	++	++	*++	+	+	++	-
Insoluble fatty acids	++	++	++	*++	--/++	-	**--/++	-
Refined petroleum								
Surdyne b140	+	++	++	*++	++	+	++	-
Exxsol D100	+	++	++	*++	++	+	++	-
GTL	-	++	++	*++	+	+	++	+
Glycols	+	--	--	++	++	++	++	**--
Ethers	--	++	-	++	--	-	-	**--
Alcohols	-	++	--	++	-	+	+	**--

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