AADE-18-FTCE-076

Hydrocarbons Separation from Drilling Waste: Mud and Cutting Treatment Using Deep Eutectic Solvents

Geir Hareland Jr., Saman Akhtarmanesh, Runar Nygaard and Geir Hareland, Oklahoma State University

Abstract

An experimental study is presented that uses deep eutectic solvent based cleaning mixture to remove all hydrocarbons from the surface of drilled cuttings before cuttings disposal when oil-based or synthetic-based muds are being used. Results are presented and compared for three different deep eutectic solvents that are environmentally friendly. Deep eutectic solvents (DES) were synthesized by mixing Choline Chloride or magnesium chloride with a hydrogen bond donor at specific molar ratios. The physical properties such as density, viscosity, and pH were measured for each of the DESs. The experimental procedure of liquid/ liquid separation was conducted by mixing contaminated cuttings with DES and Diethyl ether as an organic solvent. The two liquid phases were allowed to separate after few minutes retention time. Treated cuttings were recovered from DES layer, dried, and tested for the residual hydrocarbons content by the EPA standard static sheen test. The DESs: ChCl/Urea, ChCl/Glycerol, $MgCl_2$/Urea were compared based on their physical properties under specified conditions. The density difference between ionic solvents and nonpolar hydrocarbons results in a sharp phase separation. Based on the separation results, all solvents reduced the adhesion of hydrocarbon to calcite cuttings and drive the dissolved hydrocarbons upward into the upper layer due to the immiscibility and large density differential. The separation is completed after a very short retention time, and DESs are recoverable and capable of being re-used. By adding a small amount of water or other compatible solvents to the DESs, it is possible to alter or control some of their physical properties such as viscosity. Based on the static sheen test results, either zero or very low residual hydrocarbons content was detected on the surface of the water. Compared to the thermal desorption method which demands high capital cost and large energy consumption, using DESs shows large potential advantages in cleaning drilled cuttings both economically and environmentally. The process is simple and inexpensive; compared to the chemical or microbial treatment and thermal desorption methods, the use of DES is environmentally beneficial due to biodegradability and lower carbon dioxide (CO_2) emission.

Introduction

Typically, water-based and oil-based drilling fluids are the two generic types of drilling fluids that are used to carry out drilling operations in a safe and successful manner. One of the main functions of each drilling fluid is to carry drilled cuttings from the bottom-hole to the surface, and depending on the type of drilling fluid that is being used, cutting treatment and disposal methods for the fluids could be very different. Generally, oil-contaminated cuttings, tarnished by oil-based mud or oil-containing formations, cannot be discharged into the environment due to the fact that they impose the ecological to natural environments. Discharging cuttings in both onshore and offshore environment is highly regulated in many countries. For example, the United States EPA, as part of the National Oil and Hazardous Substances Pollution Contingency Plan (NCP), mandates zero oil discharge for drilling cuttings.

Several methods and technologies are being used for treating drilled cuttings including cutting re-injection, drying methods, thermal desorption, microbial degradation and chemical cleaning. Cutting re-injecting process includes mixing contaminated drilled cuttings, waste liquid, and other chemicals to prepare a slurry and injecting the conditioned slurry into a porous formation using the high-pressure pumps. Solid settling, low slurry displacement efficiency, tubular erosion, cutting storage, and the economics of small-scale and discontinuous cutting re-injection are only a few drawbacks of the current cleaning process (Gumarov et al., 2014 and Mkpaoro et al., 2015). Thermal desorption is a general name for the different processes of anaerobic pyrolysis separation to separate hydrocarbons from soil or solid materials by vaporizing lighter hydrocarbons using heat. High energy consumption and high capital cost of a thermal desorption plant are the main disadvantages of the process (Hagan et al., 2002). Incineration technologies that are based on oxidizing (combusting) hydrocarbons demand even more energy than thermal desorption and may produce serious secondary pollutions. Microbial degradation process involves the use of microbes, the method is focused on the utilizing the microorganisms' metabolic degradation of hydrocarbons into nontoxic components as the method of disposal (Chaineau et al., 2003). Sustaining optimal growth conditions for microbes and the low metabolic consumption rate are the main drawbacks of this method. The chemical cleaning process includes using anionic and non-ionic surfactants and other additives to wash hydrocarbons from the surface of the cuttings (Stanciu et al., 2016). In this chemical washing process, hydrocarbons are recycled by de-emulsification, however, the chemical additives in the aqueous cleaning phase are not recyclable and typically are considered a secondary pollutant.

Ionic liquids are ionic solvents that are in the liquid state below 100°C or even at room temperature. DESs are types of ionic liquids that show a substantial reduction in melting point compared to their constituting components. DESs are soluble in water and usually have higher specific gravity than water. (Abbott et al., 2004). Shuwa et al. (2014) studied the use of a DES solution for the EOR purpose. They used choline chloride/ethylene glycol to make DES, dissolved it in brine with different concentrations, and evaluated the performance of the solutions on oil displacing efficiency using sandstone samples. The authors concluded viscous forces and wettability alteration by DES are the dominant mechanisms that influence on the increase of oil recovery. Pulati et al. (2015) used a deep eutectic solvent (choline chloride and urea) with naphtha as a diluent to separate bitumen from Alberta oil sands and Utah oil sands. They used aliphatic naphtha as a diluent to reduce the viscosity of the bitumen and facilitate hydrocarbon detachment. The results were promising, however, naphtha is expensive and recycling it from other hydrocarbons is a costly process.

Leaching processes are widely used to extract different metals from solids by dissolving the metal in a suitable acid. Likewise, for the organic materials, it is crucial to choose a proper solvent to extract hydrocarbons from cuttings. In these systems, generally, large amounts of hydrocarbons in the oil-based mud are recovered by centrifugal separation system while oily cuttings and other solid materials go through leaching process to separate hydrocarbons from the cuttings. Jinzhi et al. (2017) investigated the leaching process application to treat oily drilling cuttings by formulating a new solvent that can remove diesel and surfactant from cuttings. Their system has been designed to recycle leaching solvent from hydrocarbons using a distillation process for multiple usages. The process needs multistage high-efficiency frequency converging coupling centrifugal separation.

Although much research has been done to improve and optimize the treatment of cutting and drilling fluid waste, the high maintenance cost, air pollution, CO_2 emission, operational and capital costs are still major disadvantages of the current methods. In this study, different DESs (used as separating fluids and not solvents) in combination with the leaching process were used to create a low-cost, environmentally friendly method for the treatment of drilled cuttings without decreasing the standard of cleaning expected by environmental agencies.

Methodology

Materials

The crude oil sample was obtained from a local operator in Oklahoma, produced from the Mississippian formation in Oklahoma. Sized-ground calcite was obtained from Halliburton and used as cuttings. Choline chloride with 99% purity was obtained from ACROS Organics. Laboratory grade Ethyl ether and Magnesium chloride hexahydrate with 99.5 % purity were purchased from Fisher Scientific. Glycerol with 99.7% purity and Urea with 98+% purity were obtained from BDH chemicals and Alfa Aesar respectively.

Standard Static Sheen Test (EPA Method 1617)

The treated cuttings were tested using the EPA standard test for determining whether or not cuttings are suitable for discharge. 15 grams of contaminated, wet cutting samples were cleaned using the DES-based cleaning method and then allowed to dry for 24 hours. The cuttings were then added to a container of water (12.5×12.5×9 in) with a top surface area of 156.25 in^2 (well within the EPA's range of 155.5±7.75 in^2) (Environmental Protection Agency, 2000). The surface of the water was observed for the presence of oil sheen over the course of an hour. Any observed presence of oil was recorded.

DESs Preparation

Deep eutectic solvents consist of a quaternary ammonium salt (for example ChCl) and a hydrogen bond donor (for example urea or glycerol). DESs can also consist of a metal chloride hydrate (for example magnesium chloride hexahydrate) and a hydrogen bond donor. Specific molar ratios of a quaternary ammonium salt or a metal chloride hydrate and hydrogen bond donors were mixed in a beaker and heated slowly to 100°C for 30 minutes using a hot plate. The mixture was stirred until a liquid solution was formed and then the liquid was transferred to another bottle to cool off to the ambient temperature. Three different DESs were prepared in this manner: ChCl/Urea at 1:2 molar ratio, ChCl/glycerol at 1:3 molar ratio and $MgCl_2$/Urea at 1:2 molar ratio.

Cleaning solution

Using 10 ml of each DES, three different cleaning solutions were formulated by adding 10 ml Diethyl Ether, 10 ml ethyl alcohol, and 10 ml water. Wettability alteration of cuttings and increasing differential density between the aqueous phase and hydrocarbon phase are the objectives of additions made to each DES. Ethyl ether serves as an organic solvent to wash hydrocarbons from the cuttings surface. Ethyl alcohol helps the system to quickly generate a sharp phase separation between aqueous and organic phases. Water is added to reduce DES viscosity.

Cleaning procedure

Three 10g samples of calcium carbonate (D50 = 1200) were placed in 60mL vials and were soaked in 10mL of oil for 24 hours. Then, the cleaning solution was added to the vials and they were shaken for 10 seconds. The vials were then allowed to sit for one minute before being vortexed by a mixer for another minute. The layer containing the ethyl ether and oil extract was then decanted from the vials and the layer containing water, ethanol and DES was drained. The resulting cuttings were slightly washed using water to remove the DES residue on the cuttings surface and spread out on weighing boats and dried before being tested using a static sheen test.

Results and Discussion

DESs properties

The specific gravity of the DESs was measured using a DA-100M digital density meter at 25 °C. The pH value of each DES was measured at 27 °C to 37 °C. Rheology behavior and apparent viscosity of the solvents were measured using Discovery Hybrid Rheometer HR-3 at 30°C. Table 1 shows the SG, pH and apparent viscosity results of each DES.

Table 1. DESs Physical properties

DES name	Mole ratio	SG @25 °C	Viscosity(cp) @30°C	pH
ChCl/Urea	1:2	1.194	401	7.5 @27 °C
ChCl/Glycerol	1:3	1.202	210	6.8 @25 °C
$MgCl_2$/Urea	1:2	1.399	763	4.0 @37 °C

Figures 1 to figure 3 illustrate the rheology behavior of the DESs. As shown in figure 1, which displays the rheology behavior of the ChCl/Glycerol DES, the liquid DES behaves as a Newtonian fluid.

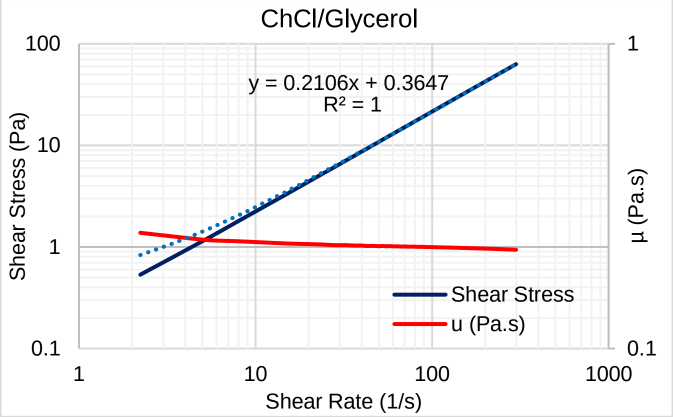

Figure 1. Viscosity behavior of ChCl/Glycerol at 30°C

Figure 2 shows the rheology behavior of the ChCl/Urea DES. The solvent, more or less, behaves as a Newtonian fluid.

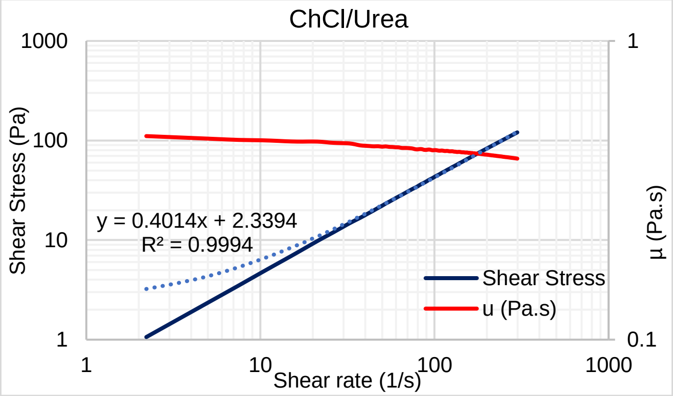

Figure 2. Viscosity behavior of ChCl/Urea at 30°C

Figure 3 shows the rheology behavior of the $MgCl_2$/Urea DES. The solvent behaves as a shear thinning fluid.

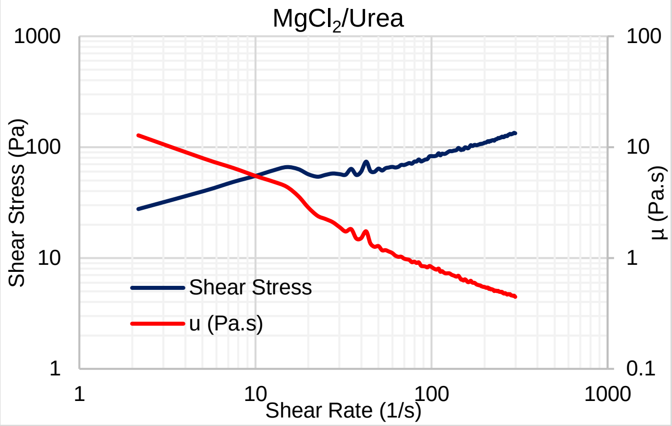

Figure 3. Viscosity behavior of $MgCl_2$/Urea at 30°C

Cleaning Results

Three samples of oily calcite cuttings were mixed with different leaching solution containing DES as separating fluid. Figure 4 shows cuttings before mixing with the cleaning solution. Upon addition of the cleaning solution, oil began to be liberated from the cutting surface rising up through the DES/Aqueous layer and being drawn up into the ether layer and some of the cuttings on the surface began to appear white again. Figure 5 shows three cutting samples moments after adding cleaning solutions.

Figure 4. Oily cuttings before mixing with the cleaning solution

After being shaken and set down, the separation of the two layers occurred after few seconds. A large majority of the oil present on the cuttings was obviously stripped away by the ethyl ether layer for each of the solutions. The DES 1 cleaning solution took longer to fully separate than the DES 2 or DES 3 based cleaning solutions initially without agitation. Figure 6 shows samples moments after agitation.

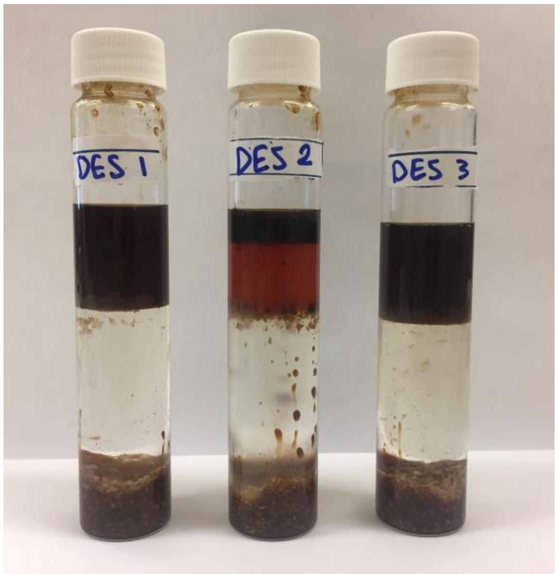

Figure 5. The DES based cleaning solutions moments after addition to oil-soaked cuttings

Figure 6. Cutting samples moments after agitation

Vortexing each of the solutions after the two minutes retention time caused immediate and visible dislodging of traces of oil remaining on the surface of the cuttings. After a minute of vortexing, all three of the cleaning solutions yield visibly cleaner cuttings. The $MgCl_2$/Urea solution yielded the most effective cleaning of the surface of the cuttings within the short timeframe. However, all of the cuttings show visible improvement after being agitated for a short time as displayed in figure 7.

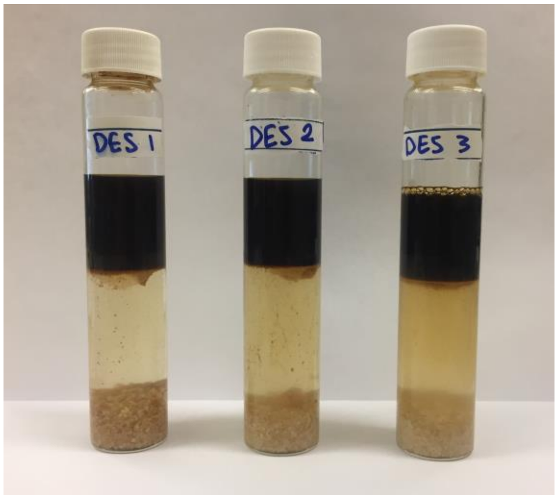

Figure 7. Cutting samples after one minute vortexing

Finally, the top ethyl ether/oil layer was decanted from the solution and the bottom water/ethyl alcohol/DES layer was removed separately. The cuttings that remained were then transferred into weighing boats. The cuttings cleaned with the ChCl/Urea and ChCl/Glycerol solutions did not appear as clean as those that had been cleaned with the $MgCl_2$/Urea based solution.

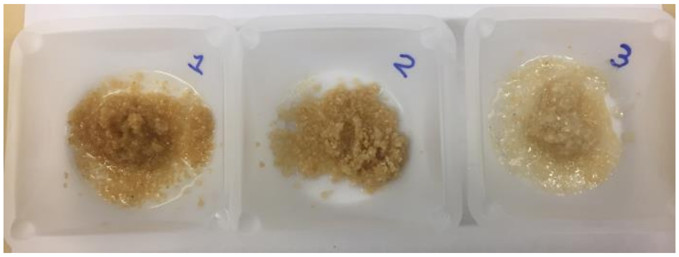

Figure 8. Calcite samples after cleaning process

The results of the Static Sheen test indicate that leaching with DES-based cleaning solutions is a suitable method for treating oily cuttings. Figure 9 shows a sheen test for the sample 3. After one hour, no trace of hydrocarbons was detected on the water surface for sample 2 and 3. Very limited trace of hydrocarbons (approximately 10 percent of the surface) appeared on the water surface for the sample 1. The results indicated that all samples passed the static sheen test.

Upon review of the cleaning process, results suggest that the $MgCl_2$-based solution was the most effective with this particular cleaning solution composition because of the rapid layer separation observed during the short retention time. Other DESs with properties similar to that of 1:2 $MgCl_2$/Urea may also be viable options for cleaning solutions. This approach to the hydrocarbons removal is a favorable one because the two layers of the cleaning solution can offer particular advantages. The DES/water layer is both biodegradable and non-toxic so it can easily be separated and reused or discarded. Because of the volatile nature of ether, the ether/oil layer should have a boiling point low enough that it can be easily separated and recycled using a small fractional distillation column. In the following section, an Aspen HYSYS simulation of such an ether recycling system is presented.

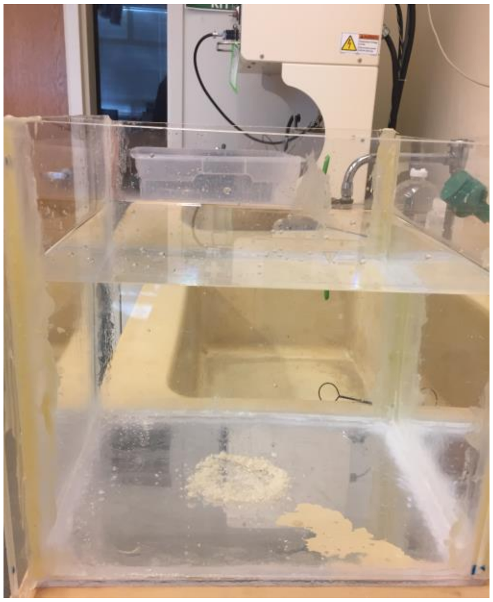

Figure 9. Sheen test

Potential Application: Aspen HYSYS simulation

As mentioned before, diethyl ether was selected as an organic solvent to remove the hydrocarbons from the oily cuttings. The boiling point of diethyl ether is 34.6 °C which makes the recycling process economically viable. The recycling process was simulated using Aspen HYSYS. Figure 10 shows the schematic flowsheet of the process. This simulation was designed for a feed stream with a flow rate of 100 kmole/hour hydrocarbon.

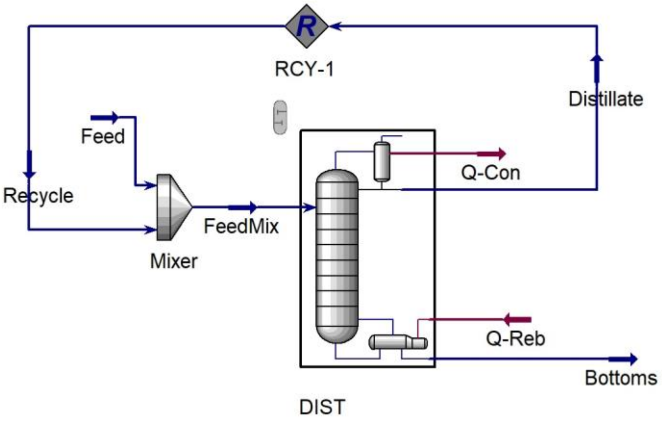

Figure 10. Diethyl ether recycling unit

Distillation column specifications and streams properties and composition are presented in table 2 and table 3 respectively. The simulated distillation column has 10 stages and the Feedmix stream, containing hydrocarbons and ether, is entered into the column on stage 5. Reflux ratio was selected 2 to reduce operational cost. Distillate stream contains diethyl ether with 99% molar purity and 99.83% molar recovery. The distillate flowrate of 30.2 kmole/hour was the minimum amount to ensure convergence of the distillation column and desired molar recovery and molar purity of diethyl ether. The temperature of the condenser and reboiler are 34.3 and 128.6 °C respectively.

Table 2. Distillation column specifications

Distillation column	Value
Number of stages	10
Feed Stage	5
Reflux Ratio	2.000
Distillate Rate	30.206
Reflux Rate	60.411
Btms Prod Rate	100.050
Comp Recovery	0.9983
Comp Fraction	0.9900

Table 3. Streams properties and composition

Stream Name	Feed	Distillate	Bottoms
Temperature [°C]	25.000	34.259	128.645
Pressure [bar]	1.000	1.000	1.000
Molar Flow [kgmole/h]	100.000	30.206	100.050
Composition	Mole fraction	mole fraction	mole fraction
n-Hexane	0.113	0.010	0.113
n-Heptane	0.113	0.000	0.113
n-Octane	0.113	0.000	0.113
n-Nonane	0.113	0.000	0.113
n-Decane	0.094	0.000	0.094
n-C11	0.094	0.000	0.094
n-C12	0.094	0.000	0.094
n-C13	0.075	0.000	0.075
n-C14	0.075	0.000	0.075
n-C15	0.057	0.000	0.057
n-C16	0.057	0.000	0.057
Diethyl ether	0.000	0.990	0.000

Conclusion

Three different DESs in combination with leaching solution were used to decrease cutting treatment cost while ensuring effective cuttings treatment. The separation process took only a few minutes and the cutting treatment results were promising. Considering the fact that only small amount of ether was used to dissolve hydrocarbons, all samples passed the static sheen test. Even though a crude oil sample was used to saturate cuttings, by centrifuging the cuttings before treatment and increasing the amount of ether, it is possible to remove hydrocarbons with much higher molecular weight. The process including mixing and agitation does not require high energy consumption. Due to the need for recycling the solvent, diethyl ether was selected to keep the operational cost as low as possible in the process.

References

1. Gumarov, S.M., Shokanov, T.A., Simmons, S., Anokhin, V.V., Benelkadi, S., and Ji, L.: “Drill Cuttings Re-Injection Well Design and Completion: Best Practices and Lessons Learned.” SPE 167987-MS, IADC/SPE Drilling Conference and Exhibition, Fort Worth, USA, March 4, 2014.
2. Mkpaoro, M.I.F., Okpokwasili, G.C., and Joel, O.F.: “A Review of Drill-Cuttings Treatment and Disposal Methods in Nigeria-The Gaps and Way Forward.” SPE 178325-MS, SPE Nigeria Annual International Conference and Exhibition, Lagos, Nigeria, August 4, 2015.
3. Hagan, J.T., Murray, L.R., Meling, T., Guo, Q., McLennan, J.D., Abou-Sayed, A.S., and Kristiansen, T.G.: “Engineering and Operational Issues Associated with Commingled Drill Cuttings and Produced Water Re-injection Schemes.” SPE 73918-MS, SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Kuala Lumpur, Malaysia, March 20, 2002.
4. Chaineau, C.H., Vidalie, J.F., Hamzah, U.S., Suripno, Asmaradewi, G., and Najib, M.: “Bioremediation of Oil-Based Drill Cuttings under Tropical Conditions.” SPE 81562-MS, Middle East Oil Show, Bahrain, June 9, 2003.
5. Stanciu, C., Fernandez, J.M., and Lambert, B.: “The Influence of HLB in Surfactants for Drill Cuttings Cleaning.” SPE 181310-MS, SPE Annual Technical Conference and Exhibition, Dubai, UAE, September 26, 2016.
6. Abbott, A.P., Boothby, D., Capper G., Davies D.L., and Rasheed, R.K.: "Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids" Journal of American chemical society, V.126, No.29, (Summer 2004) 9142–9147.
7. Shuwa, S., Jibril, B., Al-Wahaibi, Y., and Al-Hajri, R.: “Heavy-Oil-Recovery Enhancement with Choline Chloride/Ethylene Glycol-Based Deep Eutectic Solvent.” SPE 172499-PA, SPE Journal, V.29 No.01 (Winter 2014) 79 - 87.
8. Pulati N., Tighe, T. and Painter. P.: “Extraction of Bitumen from Oil Sands Using Deep Eutectic Ionic Liquid Analogues” Energy & Fuels - American Chemical Society, V. 29, No. 8, (Summer 2015) 4927–4935.
9. Jinzhi, Z., Long, L., Da, Y., Jiaxue, L., Shaojun, Z., Yuping, Y., Yushuang, L.: “Application of Comprehensive Harmless Waste Treatment Technology to Treat Drilling Cuttings in the Tian Mountain Front Block in Tarim Basin.” SPE 188263-MS, SPE Abu Dhabi International Petroleum Exhibition & Conference, Abu Dhabi, UAE, November 13, 2017.
10. United States Government: “Code of Federal Regulations” Chapter I – Environmental Protection Agency Part 435 - Subpart A - Appendix 1: Static Sheen Test. July 1, 2000.