

Chemistry in the Oil Industry XII - Abstracts

Asphaltene Nanoscience and Its Impact in the Oilfield

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Reservoir crude oils are composed of solids, liquids and gases obeying a familiar axiom about the constituents of matter learned in elementary school. Petroleum gases and liquids are amenable to chemical analysis utilizing an array of traditional and new analytical methods. Thermodynamic treatment of petroleum gases and liquids are well founded for example on variants of the van der Waals equation of state. In stark contrast, the asphaltenes have been the subject of huge debate about all but the most rudimentary properties. Ominously, published differences in asphaltene molecular weight spanned many decades with concomitant substantial variations in molecular architecture. While all acknowledged the strong tendencies of asphaltenes to aggregate, here too there had been huge uncertainties about the hierarchy of aggregation as well as aggregation numbers, structure and concentrations of formation. Consequently, fundamental limits were placed on thermodynamic treatment of asphaltenes. Working models of their phase behavior had been developed, but any 1st principles treatment of asphaltene gradients in reservoirs was precluded. A huge gradient is evident in the series of degassed oil samples from a single oil column deep water, Gulf of Mexico (courtesy: Hani Elshahawi at Shell International Exploration and Development). In recent years, a rapid coalescence of results from many different chemical disciplines has resolved many of the large controversial issues in asphaltene science, reviewed herein. The emerging picture is substantially different than conventional wisdom from one decade ago. For example, asphaltene molecular weight is mostly below a kiloDalton, thus not the giant polymeric molecules that had previously been fashionable. Many of these recent advances have been codified in a new picture of asphaltenes that builds on the 40 year old Yen model. The "modified Yen model" (also known as the Yen-Mullins model) specifies key features of the nanoscience of asphaltenes in movable crude oils. (In bitumens, larger length scale structures are expected.) The impact of this nanoscience model on the industry has been immediate. A new asphaltene equation of state, a modified Flory-Huggins equation can now treat the asphaltene gradients. By combining this new theory with a new technology "downhole fluid analysis" the huge issue of reservoir connectivity can be addressed. As shown in case studies, if the asphaltenes are equilibrated across a reservoir, it is likely (hydraulically) connected. In addition, this nanoscience model resolves a key component of tar mat formation, a long-standing problem in the industry. Moreover, this nanoscience model has been shown to apply with all three species contributing to asphaltene interfacial science, thus providing a basis for addressing wettability. Finally, the solid component of petroleum is joining petroleum liquids and gases to be understood in an increasingly proper chemical framework. The combination of new science and new technology is once again proving to be very powerful.

Application of Modern Mass Spectrometry in Oil Industry and Related Fields

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During the last 15-20 years mass spectrometry has become an indispensable method for qualitative and quantitative analysis of the most various substances: from isotopes of chemical elements to synthetic and natural polymers. It allows studying individual compounds as well as complex mixtures of thousands ingredients without any preliminary separation.

Speaking about instrumentation it is worth mentioning size reduction (instruments slightly heavier than 1 kg), an increase in resolution (up to million), and development of new methods of dissociation activation.

Inductively coupled plasma mass spectrometry (ICP-MS) gives a chance to analyze 72 chemical elements at ppt levels in a couple of seconds. The dynamic range has reached 12 orders of magnitude, allowing measuring the levels of the widespread and ultra trace elements in one injection. Any matrixes including crude oil are amenable to the ICP-MS analysis.

Electrospray and matrix assisted laser desorption/ionization dramatically increased the range of compounds amenable to mass spectrometric analysis. The sensitivity reached zepto- moles. In record cases reliable spectra were recorded with several hundred of sample molecules. Molecular masses of compounds up to dozens of millions of Daltons may be measured. Desorption Electrospray Ionization allows creation of portable devices, capable of analyzing complex biopolymers and even whole microorganisms together with small organic molecules. Alternative technique is Direct Analysis in Real Time. These two approaches eliminate sample preparation stage. Taking into account that this stage often brings to the analytical mistakes, the future of these methods is very promising. Promising results were obtained for the characterization of bio diesels composition.

Implementation of rapid GC-MS method brought to sharp reduction of time required for the analyses of complex mixtures of organic compounds. Thus at acquisition rate of 500 full spectra per second it is possible to carry out qualitative and quantitative analysis of oil fractions consisting of several hundreds of ingredients in a couple of minutes. GC-GC-MS method providing three dimensional presentation of the results, allows reliable analysis of super complex mixtures up to several thousands ingredients without preliminary fractionation. This technique is excellent in the analysis of the environmental samples. The reliable identification of the party at fault responsible for oil spillage is another feature of GC-GC-MS. ICP-MS and isotopic mass spectrometry are also extremely efficient methods for the mentioned purpose. GC-GC-MS analysis of soil samples gives a clue on the presence and composition of oil deposits deep in the ground. This method is also extremely efficient in qualitative and quantitative analysis of the most various organic compounds, including priority pollutants, oil ingredients, components of drilling muds, etc.

Application of Fourier transform mass spectrometry resulted in the notable success in the investigation of the detailed composition of the most complex natural mixtures, e.g. crude oil and oil fractions. Identification of thousands ingredients with any elemental composition may be achieved almost in automatic regime. Petroleomics was created as an independent scientific approach.

Analysis of polymers may be successfully used to identify average molecular mass, the spread of molecular masses, poly dispersion, inclusions, end groups and much more. Mass spectrometry is the best analytical technique to establishing composition and to elucidate the structure of formulations and products. This feature is indispensable in getting information required in terms of REACH. Any type of drilling muds, surfactants, corrosion inhibitors, etc are amenable to the method.

Backward and Forward in Corrosion Inhibitors in the North Sea

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The chemical application of corrosion inhibitors is a widely adopted practice in production and processing operations in the Oil and Gas Industry. Particularly challenging is the development of new chemistries, which maintain good protection of materials under a variety of conditions whilst being environmentally acceptable.

This paper will give a brief scene setting review of the history of Chemical corrosion inhibitors particularly applied to production and transportation operations and will build on work previously published on the corrosion inhibition properties of Alkylpolyglucosides (APG's) and describes its in field application to a North Sea Field, Banff, operated by Teekay Petrojarl. The paper gives detailed performance data of the chemical as a corrosion inhibitor, its environmental acceptability and additional benefits from reduced emulsion effects.

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The introduction of a Novel Environmentally Friendly Subsea Hydraulic Production Control Fluid Suitable for Use in Risk Averse Arctic Regions.

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Not many offshore wells have been drilled in the Arctic, however, what has been drilled has been productive i.e. the Snohvit field in the Norwegian Barents Sea. It is anticipated that the Shtokman field in the Russian Barents Sea, scheduled for drilling in 2016, will be extremely productive. There is great potential for exploitation of some of the most abundant oil reserves in the Arctic Circle. This can be achieved by the right market, geopolitical conditions and some investment in technological innovation.

The preservation of the unique ecosystem and biodiversity in the Arctic Circle is a highly sensitive geopolitical issue. Hence environmental issues will be taken very seriously when exploring for and producing oil and gas. It is anticipated that operators will strive to achieve zero discharge from operations that take place within the Arctic Circle. However, risk assessments indicate that it is inevitable that some discharge will occur. Therefore, it is necessary to minimise the environmental impact of discharged fluids.

In subsea production control applications, conventional hydraulic oils are not tolerated. They present inherent environmental concerns, are highly compressible and viscous at low temperatures. The current best environment and industry practice is to use monoethylene glycol (MEG) based technology. Water/MEG hydraulic fluids are incompressible, are of low viscosity and environmentally acceptable. Nevertheless it would be beneficial to use fluids with a lower environmental impact.

MEG is moderately toxic, readily biodegradable and exerts a high biological oxygen demand (BOD) and chemical oxygen demand (COD). Discharge of high BOD/COD products to the environment increases oxygen demand of marine organisms and depletion of dissolved oxygen required to sustain life. In deepwater, dissolved oxygen is replenished slowly. Decreasing BOD/COD of products will help maintain the balance of unique ecosystems in environmentally sensitive areas. An alternative formate salt freeze point depressant can be used. It is non-toxic, readily biodegradable and exerts a significantly lower BOD/COD than MEG. An 85% reduction in COD is achieved by adopting the formate salt based fluid compared to an MEG based fluid thus giving a significantly lower environmental impact. Furthermore, to achieve lower temperatures hydraulic fluids will require less formate salt compared to MEG.

In the Arctic Circle installations are likely to be on land, therefore, umbilicals are expected to be long and buried, thus demand lower viscosity fluids in order for prompt control of valves and well flow. At Arctic operational temperatures, formate salt based fluids possess significantly lower viscosity than MEG based fluids. Hence formate based fluids will have improved system and well control response. Formate salt based fluids are inherently difficult to lubricate. However, innovative chemistry has resulted in an environmentally friendly formate salt fluid that provides lubrication, corrosion inhibition and low temperature stability.

Exploiting Surfactant Synergies in the Development of Foamers for Gas Well Deliquescence

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The productivity of natural gas wells deteriorates over a period of time as a result of a loss in reservoir pressure. It may lead to flooding as a consequence of the ingress of water and hydrocarbon (condensate) from the surrounding formation. Symptoms of flooding include a drop in the gas velocity or erratic flow caused by liquid aerosols condensing and accumulating on the sides of the casing to form 'slugs' of fluid. If the liquid is not removed from the well, the fluid level and hydrostatic pressure will increase over a period of time until it reaches a point where it will effectively block the flow of gas to the surface, and from the reservoir into the well.

Well productivity can be improved or maintained by the implementation of artificial lift programmes and the preferred method will depend to some extent on well construction. These solutions include mechanical methods such as plunger and hydraulic lift, or chemical treatments, in particular Foam Assisted Lift (FAL). Surfactants or 'foamers' are an integral component of chemical formulations used in FAL to unload fluids because they are cost effective, as well as offering both environmental and performance benefits.

The aim of this paper is to describe the development of formulation strategies to improve liquid unloading by the judicious selection of surfactants. The criteria may be based on the chemistry or the molecular structure of the amphiphiles, synergies with components in the formulation or interaction with the fluids in the well bore. The properties of foams produced by commercial surfactants were studied in a series of model brine and condensate systems using both static and dynamic foam tests. Dynamic surface tension measurements provided additional information on the interfacial behaviour of the surfactants which has an influence on the mechanical attributes of the foam lamellae. The tendency of the surfactants to emulsify the model condensate was investigated since it has a bearing on whether further processing with demulsifiers or water clarifiers is required.

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New Silicone Copolymers As Demulsifier Boosters

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Crude oils from mature oilfields pose increasing challenges to demulsifier formulators. Organomodified silicones are traditionally derivatives of polydimethylsiloxanes with organic groups (often polyalkylene oxides) grafted onto the siloxane backbone, and these copolymers have been used in the petroleum industry for several years as antifoams, foamants, crude oil demulsifiers and for several other applications.

A proprietary class of copolymers has been developed in which the silicon-containing groups are combined with organic polymer backbones. These new surfactants demonstrate high interfacial activity and outstanding demulsification performance. When these copolymers are combined with organic demulsifier formulations at as low as 1-5% based on the organic actives, they act as “boosters” by accelerating the water drop, improving the interface and water clarity, and reducing the bottom sediments (BS) and residual emulsion. We will demonstrate with case histories that synergies with the new silicone chemistry can allow the use of significantly reduced concentrations of even state-of-the art organic demulsifier packages. The new emulsion-breakers may allow for the development of cost-effective demulsifier formulations and be used to solve tough emulsion separation problems, such as very heavy crudes or separation at low temperatures.

Novel Cold Flow Improvers for Waxy Crudes in Deepwater Developments

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Production and transportation of waxy crudes can pose a variety of operational challenges including wax deposition, flow problems and gelling. Increasingly operators are seeking to deploy a range of advanced additive technologies to prevent or mitigate wax flow assurance problems in preference to remedial techniques. This industry trend is most evident in deepwater projects where intervention costs or loss of production infrastructure is prohibitively expensive.

Next generation cold flow improvers will require an extended range of physical property characteristics relating to deepwater deployment, such as polymer stability and easy deployment under high pressure and/or low temperature conditions [1]. Furthermore, international regulatory regimes for the offshore oil industry will increasingly demand lower environmental impact chemistries.

This paper describes a product development project based on a proprietary polymer chemistry type, previously subject to IPR restrictions, offering significant promise for wax flow assurance management in offshore/deepwater field applications.

Following a general introduction to the polymer chemistry, and its potential as a cold flow improver for paraffinic crude oils and refined fractions, the paper will present a summary of studies based on laboratory synthesised materials with emphasis on –

- Performance testing
- Physical property characterisation
- Marine environmental assessments

In summary this polymer type has been shown to demonstrate efficacy both in wax deposition inhibition and pour point depression in a limited selection of waxy crude oils with unique physical property characteristics suited for deepwater deployment.

References

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Alkyl Polyglucosides Green Additives as Lubricant for Water Based Drilling Fluids

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The usage of surfactants as additives for lubricant in both down stream and up stream applications in the oilfield industry is well known, however, greater need for more environmentally acceptable products with better biodegradability and ecotoxicity would be the challenge to overcome, especially for offshore applications when the lubricant is added to brines for drilling operations. This paper investigates the lubricity properties of Alkylpolyglucoside as a class of 'green' surfactant in comparison to the other non-ionics surface active agents as well as their solubility in commonly used brines systems at different concentrations. The parameters which determine the suitability of such surfactants, so they can be used as lubricant and additives such as pH compatibility, temperature and acid stability as well as their solubility in different brine have been studied to provide insight in the usage of such surfactants as additives for water-based drilling fluids.

The Development and Evaluation of Substitution Free, Environmentally Friendly Combination Scale/Corrosion Inhibitor(s) for a Variety of Applications Including Subsea Systems, Through Umbilical Lines

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Oil and gas production from subsea systems is becoming increasingly more common as operators look to produce from new fields that are tied back to existing infrastructure and operate new developments in deepwater environments. Chemical injection via umbilical to these subsea systems can be crucial in maintaining integrity of flowlines and reducing the risk to flow assurance. The use of multifunctional inhibitors, in particular combination scale/corrosion inhibitors, are increasing in frequency as the operators look to achieve significant cost savings in terms of chemical consumption and process design. Using combination products minimizes potential chemical compatibility problems and fully utilizes available cores within the umbilical. Any candidate chemical must have the necessary physical properties to ensure that it can be successfully applied, whilst still protecting the integrity of the flowline and helping to ensure no flow assurance issues are encountered. The chemical must also meet stringent environmental criteria.

The product itself has to be compatible with other fluids likely to be injected through the umbilical liner and itself provide protection against the possibility of hydrate formation in the event of valve failure. This paper will detail the experimental work carried out to develop and qualify new combined scale/corrosion inhibitors, suitable for both efficacy in high temperature environments and subsea delivery. The environmental characteristics of the inhibitor will also be detailed

Evaluation tests performed on the chemistry include:-

- 1) Scaling inhibition performance testing
- 2) Corrosion Inhibitor performance testing
- 3) Umbilical suitability testing, including high pressure viscometry
- 4) Environmental testing

This paper will demonstrate that combination scale/corrosion inhibitor products can be successfully designed to mitigate risks in challenging environments whilst ensuring that all the active corrosion inhibitor and scale inhibitor components are compliant with the regulations, including the more recent CEFAS stance on surfactants.

New Approaches to Gas Hydrate Risk Management

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With the world's continuing demands for hydrocarbon based fuels and rapid depletion of "easy" fields or reservoirs, oil and gas exploration are moving to much greater deepwater and colder areas where gas hydrate formation is of increasing concern. The gas hydrate management is progressively moving away from the conventional *avoidance* (thermodynamic inhibition) towards *risk management* (Kinetic control). Low dosage gas hydrate inhibition (LDHI) is a kinetic approach attempting to inhibit and/or retard initial hydrocarbon hydrate crystal nucleation (known as kinetic hydrate inhibitors in the industry) or to prevent smaller hydrocarbon hydrate crystals from agglomerating into larger ones (known as anti-agglomerants). Compared to thermodynamic hydrate inhibitors, LDHIs are cost effective and have attracted great interest in the oil/gas industry.

This paper will describe practically new approaches for gas hydrate risk management. A new kinetic gas hydrate inhibitor was designed to offer improved compatibility with high injection temperature as well as high salinity. The gas hydrate inhibition performance has been evaluated at International Specialty Products (ISP) with high-pressure autoclaves. The results demonstrated that this newly developed KHI not only performs as good as the current commercial benchmark, poly vinylcaprolactam (PVCap), but also has high injection temperature compatibility and good tolerance to 15% sodium salt fluid system.

A novel family of anti-agglomerants have been designed and developed for high subcooling applications. The chemistries and performance will be also discussed in this paper.

Production Chemicals Based on Active Dispersions – Alternatives to Conventional Solvent Based Products

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High molecular weight polymers play an important role in many applications for the treatment of oil and gas. Examples of such polymers include but are not limited to: Polyacrylates, Polyacrylamide, Olefin Maleates, Polyalphaolefins and many Ethylene based polymers and copolymers. To allow easy handling, storage and application, most of these polymers are formulated as solutions in (most commonly) heavy aromatic naphtha, xylene, toluene, terpenes or ester-based solvents.

The low solubility of such high molecular weight polymers and their tendency to form gels at low ambient temperatures as well as the related significant increase in viscosity limits the total amount of polymer which can be incorporated into such formulations whilst still safely applied at low temperature conditions such as experienced during subsea umbilical injection or in arctic environments.

In addition the use of aromatic solvents such as HAN raises environmental concerns, whereas more environmentally friendly solvents such as terpenes, aliphatic solvents or ester-based solvents suffer either from flashpoint restrictions or solvency power limitations.

Dispersion-based products have provided an alternative to solvent based products with the most notable examples being polymers employed for drag reduction and paraffin inhibition, however stability limitations and viscosity restraints have prevented their general use. As a result particularly for application in deepwater, subsea or cold climates, low active solvent based formulations are still commonly used which require high dose rates.

Recent developments have resulted in a new generation of environmentally friendly dispersion-based products suitable for subsea injection which have been successfully applied during field trials and are now in continuous use in an increasing number of fields. This paper will discuss development, practical application and benefits of such products.

The Further Impact of REACH on the regulation of Chemicals Used Offshore in the North Sea – New challenges for 2013

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The regulation of chemicals approved for offshore use by the Oil & Gas industry in the North Sea has been carried out using the framework of the OSPAR Convention and the Contracting Parties (CPs) have implemented a Harmonised Mandatory Control Scheme (HMCS) for the approval of offshore chemicals since 2001. Following the implementation of the EU REACH Regulation in June 2007 the HMCS has been reviewed to ensure as much harmonisation between the HMCS and REACH as possible. A new pre-screening scheme incorporating REACH requirements has now been developed and implemented from January 1st 2011. This progress has been generally welcomed by the Chemical suppliers and EOSCA.

The first REACH registration deadline was December 1st 2010. So far in 2011 the impact on the offshore chemical suppliers would appear to be minimal with no significant supply issues being reported. However, there is likely to be a much greater impact on the Oil & Gas industry sector in the lead up to the next REACH registration deadline in June 2013.

This paper will review the new HMCS pre-screening scheme and discuss the implications for chemical suppliers, in the context of the work they will have to do to ensure their REACH obligations are met before the 2013 registration deadline.

REACH-Out: Chemical Communication in Complex Industry Supply Chains

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The December 2010 phase-in registration deadline for the highest tonnage and most toxic substances was a significant milestone in the implementation of Europe's most complex piece of legislation: the REACH Regulation. However, it was only really a stepping stone in the process: the longer journey of tighter regulation for the marketing of chemicals.

Having achieved the first registration deadline there seemed to be a collective sigh of relief, but this was quickly followed by the realisation that increased data availability for registered substances leads to more onerous obligations to communicate these data. Furthermore, registered substances may only be used within the constraints of published "Exposure Scenarios". These obligations lead to many questions:

- What is the best practice for effectively exchanging this information?
- How does a company identify its own uses and those of its customers (Downstream Users)?
- How and when should the uses be communicated?
- How can a company compare their required uses to those supported by their suppliers, and what options are available if there are differences?

The task would be challenging enough if all supply chains were simple and linear:

Manufacturer → Formulator → Customer

However, this is rarely the case; with multiple and alternate suppliers, numerous products, and many customers with differing expectations as far as their identified uses. There is a need to implement effective communication internally, as well as up and down supply chains. Whilst the Use Code Descriptor system outlined in the REACH guidance can help communicating uses, it does not encompass all variables and updated SDS will be required to review identified uses and the details of exposure scenarios.

This paper examines how use and exposure communications can be approached in complex supply chains to ensure that your uses and those of your customers are supported.

Refining the Exposure Assessment of Production Chemicals

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The estimation of exposure concentrations of chemicals is fundamental to evaluating the risk to the environment. Traditional methodologies used for produced water focus on the CHARM and DREAM models and are usually based upon application dosages. As such they represent a lower tier, worst case approximation of the exposure which in reality is associated with wide uncertainty bands around it. As such CHARM and DREAM provide a good screening mechanism for those substances that because of their intrinsic properties present a low hazard to the environment, but are crude tools for making decisions about the exposure of many other substances. One method of refining the exposure assessment is by assessing the residual chemicals in the produced water. Traditionally this approach has required chemical analysis of produced water streams which is technically complex and expensive. The Zonal Evaluation of Basic Environmental Discharge Encompassing Ecotox data model (ZEBEDEE) provides an interactive method of understanding how chemicals partition within the separation processes on a platform and produces residual concentrations in produced water which may be used in other models to conduct refined risk, dispersion or impact assessments. This approach is accepted by regulators and may be used to inform decisions about BAT, BEP and chemical selection. This paper will illustrate the application of Zebedee to informing real world decisions about chemical exposure from produced water.

Advances in Non-aqueous Drilling Fluid Formulations through Innovative Chemistry to Mitigate their Environmental Impact

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Non-aqueous drilling fluids (NADFs) were introduced in the late 1930s to overcome deficiencies and limitations of water-based drilling fluids. Despite the performance advantages, however, NADFs posed environmental concerns that restricted their use in many areas. Indeed, environmental and safety regulations have become increasingly restrictive since those early days, including imposition of tight standards for toxicity, biodegradability and safety that were not in place years ago. Nevertheless, it has been possible to re-design NADFs to comply with these ever-changing standards and enable continued use of NADFs.

In this paper we present newly developed concepts and designs of NADFs to overcome various environmental issues. These new technologies were made possible through innovative chemistry, such as nitrogen-free emulsifiers and unique environmentally friendly surfactants. This paper will also include the new technologies in the form of drilling fluid formulations, which can reduce the overall environmental impact of drilling operation.

Stimulation of Sandstone and Carbonate Reservoirs Using Environmentally Friendly Chelating Agent

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The objective of stimulation is to remove the damage caused to the production zone during the drilling or completion process in sandstone reservoirs, and to create channels or wormholes in carbonate reservoirs. Many problems may occur during sandstone acidizing with HCl/HF mud acid. Among those problems: decomposition of clays in HCl acids, precipitation of fluorosilicates, precipitation of aluminum fluorides caused by the presence of carbonate, silica-gel filming, colloidal silica-gel precipitation, and mixing between various stages of the treatment. Mud acid may cause significant damage to sandstone reservoirs, especially for those with high calcite content.

In this study a recently introduced environmentally friendly chelating agent, glutamic acid-N,N-diacetic acid (GLDA), was used to stimulate sandstone and calcite cores. Different types of sandstone and calcite cores were used such as Berea sandstone and Indiana limestone and various pH values (1.7, 3, 3.8, 11, and 13) of GLDA were used. The cores were X-ray CT scanned before and after the treatment to investigate the effect of GLDA on the cores. The effluent samples were analyzed for total GLDA, and for calcium, magnesium, aluminum, and iron using ICP showing the ability of GLDA on the complexation of these ions. Coreflood experiments were run at temperatures ranging from 200 to 300°F.

GLDA showed a significant ability to chelate calcium, magnesium, iron, and aluminum ions from the sandstone cores and in creating wormholes in calcite cores. At 300°F GLDA (pH = 3.8) was able to enhance the core permeability from 100 to 200 md. X-ray CT scan showed a porosity increase after the treatments. GLDA proved to be thermally stable up to 300°F in the coreflood experiments. Also, GLDA showed good results in biodegradation tests, in which more than 80 wt% was degraded by natural bacteria in less than 28 days. Based on the results obtained, GLDA can be used to stimulate sandstone and carbonate formations up to 300°F. GLDA is biodegradable and can be used to stimulate offshore and onshore wells.

Low Oil-Water Ratio Invert Drilling Fluids: Taking Emulsion Performance to the Edge.

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There are significant environmental and cost advantages to be had by the use of low oil-water ratio (OWR) low-toxicity (LTOBM) and synthetic (SM) muds. Conventional oil-based drilling fluids, typically with an OWR between 60:40 and 90:10, exhibit solid performance over a wide range of downhole conditions. However, at oil-water ratios below 50:50 the emulsion properties of the fluids start to become critical for performance. The role of droplet size and interfacial tension on the development of rheology in invert systems, together with the changes in phase and emulsion stability have been studied over a wide range of oil-water ratio. The results are discussed in terms of the competing forces observed under the flow conditions present in a wellbore. Some of the advantages of the new emulsifier and viscosifier chemistry that has been developed for these systems are discussed.

Laboratory Simulation of Scaling in the Presence of Hydrogen Sulphide Scavengers

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Hydrogen sulphide scavengers are liable to cause calcium carbonate scaling when dosed directly into produced water streams or when used in gas treatment equipment from which condensed water is routed into produced water streams. The addition of a base (when using conventional triazine based scavengers) increases the alkalinity of the water and the pH rises. This can change a non scaling system into a severe scaling system. The presence of excess carbon dioxide can buffer the pH down towards 6, but results in the bicarbonate level increasing.

We have developed static and dynamic test methodologies to assess the impact of hydrogen sulphide scavengers on scaling for situations for both low levels of carbon dioxide (e.g. oil fields) and high levels of carbon dioxide (e.g. gas production fields). We show that how the scavenger and carbon dioxide are treated in the laboratory has a significant impact on the results and needs to be based on the fluid flow in the field.

We have used these laboratory methods to investigate the effect of different scavengers, changes in the topsides design , and the effectiveness of different scale inhibitors in the presence of hydrogen sulphide scavengers.

Structure and Function of Asphaltenes: A Geochemical and Ultrasound Study

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Asphaltenes are well known to be the most important components causing blockages in oil pipelines and fouling in refineries which lead to enormous costs. They are also responsible for the formation of tar mats in petroleum reservoirs, which can impede crude oil recovery (Wilhelms and Larter, 1994). Despite the amount of effort that has been expended on studying these nanoparticles there is still a great deal of debate surrounding a number of their fundamental properties. For instance there is the question of whether the solution behaviour of associating molecules better explain the features of asphaltene-containing systems, where the high viscosity of bitumen and asphaltenic mixtures is related to their proximity to the glass transition (Sirota, 2005), or is the colloidal model the more useful one in establishing structural features of asphaltene aggregates including their shape and size? In this presentation we integrate petroleum geochemistry with ultrasonic spectrometry and microscopy to gain new insights into the aggregation properties of asphaltenes.

Our working hypothesis is that the asphaltenes, under certain conditions of solvent, ionic strength and type of ion, form vesicles and that the swelling of the vesicles by solvent increases the volume occupied by asphaltene particles. A glass transition may then occur due to excluded volume effects amongst the particles (e.g. Tanaka, 2000). These differences in asphaltene properties are supported by the ultrasound spectrometry of these three sample types. When we diluted fresh North Sea oil with 50% toluene, we observed that the oil, when swilled around the walls of the glass container had a grainy appearance. In the spectrometer sample cell, as the sample levels went up and down it left rivulets of oil streaming down the walls (see inset to Fig. 1). This indicates phase instability. The attenuation spectrum contained breaks and departures from the normal power law dependence (see ▲ in Fig. 1). Where the curves depart from power law dependence, this indicates that the samples change DURING a single frequency sweep. The fresh crude oil therefore shows clear signs of a changing size of the scattering entities. In contrast, the toluene diluted biodegraded oils and bitumen (including the isolated asphaltenes) behave exactly like the toluene in which they are suspended, indicating that in this case no measurable excess scattering was occurring. These results demonstrate the potential that lies in bringing together the normally disparate disciplines of organic geochemistry and ultrasonic spectroscopy in order to improve our fundamental understanding of the asphaltene fraction.

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Introducing a New Approach to Aid Optimisation of Corrosion Inhibitor Dosing

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Data from monitoring production chemicals in produced fluids are currently used to support decision making on what chemical to use, when to use it and how much of it to use. Improvements in chemical monitoring, in terms of accuracy and time to result could aid in optimising dosage. For corrosion inhibitors specifically, optimising dosage may have financial implications, consequences for asset integrity and process optimisation particularly oil in water separation.

Results of the testing of a new tool being developed to aid corrosion management will be presented. In the approach, identification of the optimum functional dose of inhibitor to protect against general corrosion is determined by the presence of inhibitor micelles in samples. Micelles are molecular aggregates of the surfactant actives within inhibitors that form at the critical micelle concentration (CMC) and previous studies have shown that optimal inhibitor performance is achieved at this concentration. A photonics-based detection system will be introduced and compared to traditional corrosion testing methods. In addition, data on how different inhibitors, crudes, brine compositions and environmental conditions impact the amount of active available in the brine to inhibit corrosion will be shown.