

Abstracts of Papers to be Presented at to Chemistry in the Oil Industry XI

REACH Pre-Registration at Baker Hughes - A Case History

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In December, 2006 the European Union enacted the most significant piece of legislation imposed on any chemical industry in recent times: 'REACH' (Registration, Evaluation, Authorisation and Restriction of Chemicals). While a register of chemicals in use in the EU already existed, a 1999 study of High Production Volume chemicals had revealed that toxicology data sets were complete for only 14% of these materials and 21% had no toxicology data at all. This data gap and increasing public concern over chemical exposure has led to the requirement that the industry submit a full toxicology data set on every chemical substance manufactured or imported into Europe in volumes greater than 1 MT per year.

Where more than one entity imports or manufactures a given chemical at greater than 1 MT per year, the potential registrants are required to co-operate in a Substance Information Exchange Forum (SIEF) to ensure that existing eco-tox data is shared and further mammalian testing is minimised. Registrations are then to be submitted to a phased timetable over the next decade. However, to gain access to this phase-in period and to ensure that potential registrants were assigned to the correct SIEF, pre-registration with the European Chemicals Agency (ECHA) was required. Between 1st June and 1st December 2008, ECHA received 2.75 million pre-registrations.

Submission of a REACH pre-registration requires the identity of the chemical to be declared. Under previous regulations this requirement could be satisfied by studying a register of pre-existing chemicals and assigning the most appropriate registry number to each substance.

REACH requires the identity assigned to each substance to be justified with analytical data. Extensive guidance has been issued on how to fulfil this requirement. The complex nature of many of Baker Hughes' products has required a rigorous investigation of the chemical species present. Describing products in this way contrasts with common practice, which has been to describe products by their performance as corrosion inhibitors or demulsifiers, etc.

The obligations of a chemical manufacturer or importer under the REACH legislation are dependent on their position in the supply chain and on the nature of the chemical concerned. Baker Hughes' product range includes polymers and non-polymeric substances, EU imports and exports, as well as blends and re-labels of purchased materials. In total *circa* 1,000 products are affected. Having gained a general understanding of the pre-registration responsibilities for the product types classified above, a team involving technology personnel from all divisions of Baker Hughes was established and a comprehensive review of each product line was undertaken. Products fitting the REACH definition of a polymer are exempt from registration. However, proving that this was the case for certain low molecular weight polymeric materials presented a particular challenge. Baker Hughes' approach to these materials will be discussed.

Communication of substance identity along non-EU supply chains prior to import also proved problematic. The required exchange of compositional information led to tension between commercial interests and regulatory requirements. Examples will be given and some of the difficulties associated with chemical supply into Europe will be discussed.

Novel Chemical Solutions to Unusual Oilfield Scale Challenges

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The control of inorganic scales by chemical inhibition and removal has been developing over the past 40 years with more effective inhibitor chemicals working at lower treatment rates and dissolvers working more rapidly.

The improved mechanistic understanding of chemical inhibition and retention for squeeze application has led to improved chemistry and application methods being developed. This paper presents laboratory and field results on the evaluation of a non acid carbonate scale dissolver and the development work on a combination halite/carbonate and sulphate scale inhibitor.

The challenge of developing an effective carbonate scale dissolver that did not rely on simple low pH acid dissolution (HCl, formic acid, acetic acid) but on effective chelation will be described. This eliminates the risk of corrosion reactions to downhole tubing associated with conventional acid dissolver applications. The non acid dissolver formulation has been applied to formations in South America which had shown a history of damage following conventional acid cleaning treatment and data will be presented that show pre and post treatment well performance.

The formation of halite scales and associated carbonate scale is an issue in many gas fields and in HP/HT condensate fields within the North Sea and North Africa. Development work on a novel polymer, which offers both halite and conventional scale control, will be outlined. The advantages of a molecule which can control halite, carbonate and sulphate scales rather than a cocktail of chemicals in a formulation will be outlined in terms of scale squeeze and continual injection applications

The continued drive for more environmentally acceptable chemistry has also been taken into account during the research into the two products outlined above and both meet and exceed the current North Sea regulations.

Laboratory Examination of the Factors Influencing the Formation of Silicate Scales Under Oil Field Operating Conditions

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The formation and prevention of common inorganic oilfield scales such as barium sulphate and calcium carbonate has been extensively studied, and while some challenges remain, the factors controlling such scale deposition are now quite well understood. However, even when such common scales are controlled, the formation and deposition of less well understood mineral scales can adversely affect production.

Recently, unexpected silicate scale deposition incorporating magnesium and iron was detected in two production systems operated by Talisman in the UK North Sea. To prevent production issues occurring later in the field life due to the continued deposition of these silicates, a laboratory investigation was conducted to examine the formation of silicate scales under conditions closely replicating those in the field. By examining the influence of brine chemistry, pH and temperature on the formation and composition of these scales in the laboratory, a better understanding has been gained of both the field behaviour of the scaling brines and the options available to limit or prevent field deposition in the future.

A Technology Platform for Designing High Performance Environmentally Benign Scale Inhibitors for a Range of Application Needs

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Environmental legislation and waste water discharge regulations have significantly limited the number of scale inhibitor technologies that can be applied in OSPAR countries and those operating similar regulations in environmentally sensitive waters globally. Whether due to their toxic nature or lack of biodegradability, technologies that were until recently widespread (such as pentaphosphonates) are now no longer used, or are limited to applications where no viable alternative has yet been found.

A number of new scale inhibitor technologies have been introduced in recent years to try and fill this performance vacuum. These have been based on natural or synthetically produced natural analogues that offer some performance, but have had not offered the utopian ideal in terms of performance or applicability, limited as they are by the density of the functional groups on the polymer backbone and a limited ability to vary molecular weight.

Based on the highly variable nature of oilfield produced waters, scales and application conditions, it has long been realised that a broad portfolio of products is required to satisfy all the scaling needs of the market.

AkzoNobel introduce a newly developed chemical approach that offers release from these performance limitations, and has the ability to be broadly developed to meet a range of application needs. Whilst the technology offering are environmentally benign the platform development can be carefully chemically manipulated and modified to meet a broad range of applications needs, as well as providing products with a reduced dependence upon non-renewable, fossil-fuel derived raw materials.

The process of manufacture of the new hybrid polymers will be presented in which a free radical is induced in a natural polysaccharide from which a synthetic polymer can be grown under standard free-radical polymerisation conditions - allowing molecular weight, functional-group density and type to be accurately controlled. Further to this, performance data will be presented for these hybrid products that show whilst a significant portion of the synthetic component of the polymer has been removed, the performance is little affected under standard application conditions. Hybrid product performance will be baselined against standard synthetic polymers used today, common phosphonates and natural polymers.

We will show that whilst providing a range of high performance, environmentally benign scale inhibitor variants, the hybrid technology also provides some unexpected and very useful benefits, such as brine tolerance, resistance to iron (II) contamination and in some cases the ability to blend into solvent solutions to provide liquid products for cold temperature climates.

Also disclosed will be full environmental data that show the technologies to meet (and hopefully in coming generations, exceed) the yellow status required for Norwegian sector North Sea applications.

Issues that may be relevant to the applicability of the technology will also be addressed, including thermal stability in use and bio contamination resistance - particularly important for squeeze application and PWRI.

Secondary benefits that will be explored in the coming months to help support the papers content will be delectability and adsorption of the polymers on silica substrates (dynamic and static tests).

Suggestions will also be given for hybrid scale inhibitor/corrosion inhibitor formulations that have been shown to be mutually compatible in our internal testing

Whilst in the early stages of development, it is felt that this technology platform provides a novel approach to an increasingly severe limitation of existing technologies to resolve standard oilfield scales.

Gel Systems with Properties Suitable for Remediation of Water Injection Wells with Performance Impaired by Fractures and Super-permeability Zones

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Low toxicity commercial polymers with properties suitable for remediation of water injection wells rendered inefficient by contact with fractures or super-permeability zones were investigated. Thermally-induced, reversible gelation characteristics of ABA-type ethylene oxide (EO)- propylene oxide (PO) copolymers were studied; specifically, the properties of an $EO_{21}PO_{47}EO_{21}$ tri-block copolymer of molecular weight 46000 were studied for temperatures relevant to certain BP applications. Copolymers of this type exhibit complex phase behaviour with the temperature-related formation of up to two distinct gel phases. A soft gel forms in the region of 60 to 70°C at relatively low polymer concentrations. The results of constant shear and oscillatory rheological studies are reported here, including the effect of polymer concentration on the formation and properties of the soft gel. The effect of temperature changes and thermal cycling on the gel were also included. The results are interpreted in terms of the potential use of such a gel in improving water flood sweep including equations to predict stability and the onset of movement in fractures and matrix.

Modification of Relative Permeability in Wet Wells in Sandstone Reservoirs: Multiple Well Treatments and Core Experiments

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In a previous paper presented at the Symposium VII, the basic development of a means of treating a wet sandstone well to adjust the relative permeability away from water was described.

Since then, multiple tests have been carried out on the wells in a Canadian Field with the aim of showing that additional oil is recovered not just accelerated production. In parallel, a programme of has been carried out on model sandstone cores (Clashach sandstone) to elucidate the behaviour of the hydrophobic material in a sandstone reservoir.

The results of the work will be presented and analysed and conclusions will be drawn about the applicability of this method of increasing oil production through treatment of producing wells.

Development of a Novel Fracturing Fluid for Applications in Russia

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The objective of reservoir stimulation is to enhance the faster delivery of hydrocarbons and to increase the ultimate recovery of hydrocarbons. Usually, the stimulation of oil and gas wells is performed by hydraulic fracturing operations creating high conductivity channels enabling increased hydrocarbon production.

A fracturing fluid plays a critical role in fracturing operations; initially by opening the fracture and subsequently transporting and distributing the proppant along the length and the height of the fracture. Typically, key parameters characterizing fracturing fluids are viscosity (for the transport of proppant), tolerance towards shear created by the placement of the fracturing fluid, and temperature stability. In addition, these fluids must break and clean up efficiently after the treatment, provide good fluid loss control, exhibit low friction pressure, be economically practical, and be operationally simple.

The development of a new borate based fracturing fluid including its applications is discussed. Despite the fact that borate based fracturing fluids have been in common use for several decades, we introduce a fluid that has significant advantages with respect to polymer loading and operational simplicity over the existing technology. The presented fracturing fluid is based on guar with a novel borate-based cross-linker. The cross-linker is a solid chemical, which due to its chemical and physical properties allows reliable and shear stable cross-linking characteristics.

In this paper we will discuss the fluid's development and optimization for various well conditions typically encountered in Russia. We will also emphasize the fluid's environmental and handling properties in cold climates.

We also present the results of conductivity experiments simulating typical fracturing environments during placement and flow-back periods.

Keywords; oil spill, natural attenuation, remote sensing, remediation, prediction.

Design of Highly Inhibitive Water-Based Drilling Fluid for Environmentally Sensitive Land Drilling Applications

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This paper describes a new highly inhibitive water-based drilling fluid developed for water sensitive shale drilling in environmentally sensitive land drilling locations. The new highly inhibitive fluid eliminates salt, which is a major concern for environmentally sensitive land locations. This fluid provides more effective shale inhibition, environmental benefits and economic advantages over existing drilling fluid systems for land drilling (onshore) applications.

The majority of drilling problems are attributed to water sensitivity of shale and to combat the drilling problems associated with shale, numerous high-performance water-based drilling fluids have been developed and applied in the field. However, many of these drilling fluids depend on some form of salt for optimum performance, which limits their use in environmentally sensitive areas for onshore (land) drilling applications. Salt-containing drilling fluids require additional processing or more expensive disposal to prevent contamination of soil and groundwater.

We have developed a high-performance water-based drilling fluid, which does not depend on salts for inhibition. The environmental benefits of the high-performance water-based drilling fluid, which provides high levels of shale inhibition in a freshwater drilling fluid, will be presented. The toxicity and the drilling waste disposal implication of this system for land use are considered, and comparison of the drilling performance properties with other currently available fluids will be shown. The chemistry and the formulations of the drilling fluid will be highlighted.

New High Injection Temperature Kinetic Hydrate Inhibitors

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Kinetic Hydrate Inhibitors (KHI) have been widely employed in the petroleum industry as a cost-effective and environmentally friendly method to prevent gas hydrate formation and provide flow assurance in gas production systems. KHIs usually consist of water-soluble polymers which delay the nucleation and growth of gas hydrates. For these polymeric KHIs, the injection temperature is a critical issue for their successful field application. With the increasing demands of oil and gas production, there has been a significant increase in the need to develop products suitable for higher chemical injection temperatures. As such, oilfield service companies are requiring gas hydrate inhibitors that can be injected at temperatures of 70 to 90°C to offer for tender. This paper presents the recent research efforts of International Specialty Products (ISP) to develop high injection temperature KHIs. A series of polymers were designed and synthesised to have a cloud point of at least 85°C. The hydrate inhibition was evaluated in-house

with high-pressure autoclaves. The results indicate that some inhibitors with optimized composition are not only compatible with an injection temperature higher than 85°C but also have a hydrate inhibition performance comparable with a current leading commercial inhibitor.

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Structure-Property Relationships for Novel Low-Alkoxylated Corrosion Inhibitors

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Fatty amines, alkoxylated fatty amines, amidoamines, imidazolines and quarternary ammonium compounds are examples of chemical classes frequently used as bases in corrosion inhibitor formulations for oilfield use. Considering the mechanism for how these products carry out their task, i.e. by forming a film protecting the steel surface, it is natural that the exact structure of the molecules will have an impact on the final performance. Although the conditions are usually varying for each real-life case, calling for different chemistries to be used, the choice of product is still facilitated by basic knowledge regarding the relative performance within different chemical classes.

This paper will discuss structure-property relationships for low-alkoxylated amines and amidoamines as well as low-carboxymethylated substances of the same classes. The compounds have been evaluated as (oilfield) corrosion inhibitors by ellipsometry to monitor adsorption as well as LPR techniques to demonstrate corrosion inhibition potential. Possibly also some QCM-D data can be included. With this technique information on adsorbed amount linked to surfactant aggregate structure can be obtained. Correlated with corrosion rate measurements this method may give valuable information for structure optimization. Environmental/regulatory aspects for the products will be treated as well.

An introduction to further novel products fulfilling requirements for use without substitution warning in British and Norwegian sectors of the North Sea may (depending on the progress of the intellectual property process) be given.

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Gap Analysis of the OSPAR's Harmonised Mandatory Control System and EC Registration Evaluation Authorisation and Restriction of Chemicals Regulations (1907/2006)

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An important question for the offshore industry is what will be the regulatory burden under HMCS as the timetable for REACH progresses. As part of Cefas' work for DECC a GAP analysis for the HMCS and REACH has been conducted to aid discussion on this key issue. The objectives of this work were to identify the areas of HMCS that may be easily harmonised with REACH, as well as identifying those areas currently covered by HMCS, which REACH does not cover. In this paper we present the results of the gap analysis and try to answer some of the questions about implications of REACH for the HMCS.

The Impact of REACH on the Regulation of Chemicals used Offshore in the OSPAR Convention Area - Another Chance for Harmonisation?

Ian Still, Champion Technologies

REACH is the Regulation for Registration, Evaluation, Authorisation and Restriction of Chemicals. It entered into force on 1st June 2007 to streamline and improve the former legislative framework on chemicals in the EU. It makes industry bear most responsibilities to manage the risks posed by chemicals and provide appropriate safety information to their users.

REACH requires all manufacturers or importers of chemical substances in quantities greater than 1 tonne per year to submit a dossier for registration to the European Chemicals Agency (ECHA). The registration process will result in authorisation of those substances of very high concern (SVHC) limiting those to specific uses or requiring their substitution with substances less harmful to health and the environment where possible.

The regulation of chemicals used by the offshore Oil & Gas industry in the North Sea has been carried out using the framework of the OSPAR Convention and the Contracting Parties have implemented a Harmonised Mandatory Control Scheme (HMCS) since 2001. This paper will compare the regulatory approaches of REACH with the HMCS and comment on the future regulation of the chemical supply industry as REACH becomes fully implemented.

The Impact of Active Compound Application Methods on the Validity of Ecotoxicity Study Data

Max La Vedrine, Edward J. Smith, Anthony Millais, Louise Mann, Denise Doran, Lynn Jones, Bob Rowles and Steven Supple, CefaS

With the onset of the new REACH guidelines within the European community renewed focus has been placed on the adequacy of OECD based studies, which form the basis for data collation with which to perform risk assessments. The Offshore Chemical Notification Scheme (OCNS) Offshore Chemicals database holds standardised ecotoxicological data, for over 6,000 chemicals used by the Oil & Gas Industry in UK and NL waters. We collated data for 1 compound found in over 100 products the database yielded a total of 460 ecotoxicological endpoints for 10 different species, although dominantly *Acartia tonsa*, *Skeletonema costatum*, *Scophthalmus maximus*, and *Corophium volutator* which allowed for a direct comparison of ecotoxicological endpoints. We reviewed the impact of active ingredient application methods on the variability of the eco-toxicological data. Our results identified possible issues with study design, which caused high levels of variability. From a regulatory standpoint this variability could result in differing OCNS hazard banding and HQ calculations, furthermore this type of issue will be an important one for SIEFs to deal with as part of their REACH registration. We present an overview of our data and discuss the implications and possible solutions to the problems we have highlighted.

The Development of the EOSCA Generic Exposure Scenario Tool (EGEST) - Why we need it? The development of a method to conduct a generic exposure scenario for offshore chemical use to enable REACH registration

Graham Payne, EOSCA Secretary; Ian Still, EOSCA Chairman; Nik Robinson, BMT Cordah; Steve Groome Rhodia UK Ltd.

REACH is the Regulation for Registration, Evaluation, Authorisation and Restriction of Chemicals. It requires manufacturers and importers of substances to provide a defined set of information, in the form of a registration dossier, to the European Chemicals Agency.

Following registration, downstream users (DU) will receive information on dangerous substances and preparations, including risks from their use and measures to control these risks, in safety data sheets. Some safety data sheets will have an annex, called an exposure scenario which will give more specific information on how to use the substance or preparation safely and how the users can protect themselves, their customers and minimise environmental risk. Uses need to be shared up and down the supply chain to ensure that end uses are included in the Registration Dossier submitted to ECHA. Uses not covered will not be allowed.

The majority of substances used offshore by the Oil & Gas industry are expected to be used onshore in similar or different use categories. However, there are likely to be substances that are used exclusively offshore, and some of these are used in relatively large quantities. In order

to facilitate the development of appropriate exposure scenarios an industry initiative involving the European Oilfield Speciality Chemicals Association (EOSCA) has proposed a standard approach to developing use and exposure scenarios which will be used in the chemical safety assessments. This paper will outline the development of a generic approach to exposure scenario modeling and demonstrate the EOSCA generic Exposure Scenario tool (EGEST).

Green Polymers for the North Sea

Stefan Frenzel, BASF Global Oilfield Solutions, Germany

In the North Sea region the use of non-biodegradable chemicals in off-shore operations becomes more and more restricted. For organic chemicals with a biodegradability of less than 20% a substitution warning is issued in the Norwegian sector.

In order to serve the need for biodegradable additives for the exploration and production of oil and gas we followed a new synthesis approach towards highly efficient and new biodegradable polymers in different application areas (drilling, cementing and production).

Many attempts so far to manufacture "green" chemicals either resulted in low performing products or their biodegradability was simply too low.

Our polymers exhibit a high biodegradability (OECD 306) and keep their efficiency because of their flexible, tailor made chemistry.

In this presentation we will introduce new and efficient polymers which are performing well in the different application fields: Drilling (Fluid Loss Additives), Cementing (Dispersants) and Production (Kinetic Gas Hydrate Inhibitors).

Progress Towards Biodegradable Phosphonate Scale Inhibitors

Henry C. Fisher, Andrew F. Miles, Scot H. Bodnar, Steve D. Fidoe and Curtis D. Sitz, Champion Technologies

The key environmental requirements for offshore chemicals used in the North Sea and surrounding waters are incorporated in the Harmonized Mandatory Control Scheme (HMCS) requirements of the OSPAR Convention*. The OSPAR Convention has been signed by a number of countries including the UK and Norway and is intended to harmonize the environmental approval required for chemicals used and/or discharged offshore within the OSPAR area. In short, the Convention requires a standard environmental data-set for each chemical substance with test results from approved laboratories accredited to Good Laboratory Practice (GLP). The data required for each substance includes results for biodegradation, bioaccumulation and toxicity.

Until relatively recently, highly functionalized phosphonate scale inhibitors have been widely used for the control of oilfield scale within the OSPAR area. These products can offer a number of benefits including acceptable cost, high efficacy versus a range of carbonate and sulphate

scales, good retention during squeeze application and ease of analytical detection. Phosphonates are also typically non-toxic and non-bioaccumulative. Unfortunately, the biodegradation of many of these products is poor. The recognition of their limited biodegradation, especially by marine protocols such as method OECD (Organization for Economic Cooperation and Development) 306, has made many of these products environmentally unacceptable, when assessed for the HMCS.

This paper presents a selection of work performed to study the biodegradation of various scale inhibitors including phosphonates. Testing of selected monophosphonates, not traditionally used in oilfield applications but reported in the wider literature to undergo biodegradation in certain environments, demonstrated that phosphonates can show acceptable biodegradation by approved marine protocols. Based on this finding, further work was performed including the examination of a number of mono, di and higher phosphonates of various structures. Work on a novel family of phosphonates that show useful performance versus some scale types, while also consistently showing 20 - 60% biodegradation by OECD 306 in 63 days, is also described.

Applying Biochemistry Concepts to Oilfield Produced Fluid Monitoring: A Focus on Latently Detectable Tags and Tracers

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Oilfield produced fluids are complex mixtures of hydrophobic and hydrophilic entities: as such, sensitive and specific analysis is a challenge, particularly in the field. Biological systems also contain complex fluid mixtures and like oilfield systems can be harsh environments. However, by exploiting nature's highly specific chemical recognition systems, analysis of these mixtures can be simplified; for example, biochemistry-based techniques often use simple spectrophotometric measurements and do not usually include laborious separation procedures.

We have conducted a study to investigate whether biochemical concepts, such as the use of small biomolecule as tags and tracers, can be applied to the analysis of oilfield additives.

Applications of this concept include:

- Tagging difficult to analyse polymers such as sulfonated scale inhibitors;
- Monitoring concentrations of treatment chemicals, such as scale inhibitors, from co-mingled streams;
- Onsite analysis using simple spectrophotometric techniques;
- Tracers for oilfield fluids; avoiding the use of radioactive substances.

Scale inhibitors have previously been tagged using fluorescent groups and a number of fluorescent tracers are available. However, the disadvantage of using fluorescent tags and tracers are that their analysis can suffer from background interference caused by the inherent

fluorescence of produced water as well as poor limits of detection. The advantage of using latently detectable biomolecular tags is that they are only detectable upon addition of a specific reagent and any background fluorescence can be subtracted before the detection reagent is added. The compatibility of these tags with synthetic seawater, produced water, treatment chemicals, crude oil and solutions of various pH and temperature was investigated. We have identified multiple tags that are detectable to low ppm values, can be differentiated in the same sample and which are stable under a range of difficult conditions.

This work shows that biochemistry concepts can be applicable to oilfield produced fluid analysis and lend themselves to the development of simple, highly sensitive, quick detection assays that can be used on-site; providing near real-time information to Operators and allowing them to make timely, informed decisions, especially where time is critical and delays in instigating treatment regimes risk well closure and loss of revenue.

Challenges Facing Residual Chemical (Polymer) Scale Inhibitor Assay in Oilfield Waters

Kirsty Marshall, Gordon Graham, Ian Munro and Marjorie Smillie - Scaled Solutions Limited

With the move over the last 10+ years towards more environmentally acceptable "green" oilfield chemicals has come a general move away from conventional phosphonate based scale inhibitor use in both the Norwegian and UK sectors of the North Sea. This in turn has led to an expansion of the number and diversity of polymeric species, in particular sulphonate polymer species, being employed for both in downhole squeeze applications. With this however comes a number of known difficulties in their residual assay, especially for sulphonated polymers where separation of the inhibitor from the brine phase can be a time consuming, labour intensive and often difficult operation. In order to overcome these known difficulties, a number of tagged species such as the "P" containing polymers have been marketed in recent years which offer the benefit of effective inhibition together with a more readily detectable "tag".

However the ability to assay a particular moiety within a polymeric scale inhibitor does not necessarily mean that accurate chemical analysis can be routinely achieved, even supposing that the chemical can be effectively separated from other interfering impurities. This partly relates to the presence of other interfering species often present in produced waters but also to the chromatographic nature of the reservoir rock matrix which means that following a squeeze treatment different parts of the polydisperse injected inhibitor (all polymers are polydisperse to some degree and therefore contain a wide range of molecules differentiated by their molecular weight i.e. polymeric scale inhibitors are by their nature mixtures of components). In short the paper will illustrate the different residual inhibitor assay's which can be recorded for different analytical techniques based on which part of the polymer is being assayed. In summary results are shown for analysis of selected polymers by different known techniques showing order of magnitude differences depending on the particular assay technique adopted following retention / release (e.g. adsorption / desorption or precipitation / re-

dissolution) reactions with reservoir substrates. To confirm the most appropriate detection method, performance tests are then examined which indicate which methodology is more applicable for the particular situation. The goal here therefore is not to be able to assay the brine system for a particular component per se, but to be able to detect accurately the concentration of "active inhibiting scale inhibitor" present in the brine system. Finally, in order to improve on the analytical techniques a number of semi automated and fully automated HPLC techniques have been described recently within the industry, several of which build on similar techniques presented at this conference in 1995. This paper will also therefore present results from the development of our own HPLC techniques and compare the results obtained directly with those obtained from a range of different "bench - top" wet chemical techniques as well as, where appropriate, obtained through automated ICP techniques. Results of all techniques are verified (or not) by examining the inhibition performance, based on the *apparent* concentration determined by the particular assay method. In short the paper therefore describes with examples several of the known limitations of polymer assay in oilfield produced waters. It illustrates how different *apparent* concentrations can be determined with different analytical techniques due to chromatographic separation within the reservoir (in addition to the presence of interfering impurities) and illustrates which methodologies detect the active scale inhibitor component of a particular polydisperse polymer mixture. The procedures examined in this paper are all however based on conventional analytical approaches which are currently used within the industry and therefore the paper illustrates the risks should a single analytical approach in oilfield waters.

Clay Swelling Inhibitor Structure-Activity Relationships: a Combined Molecular Simulation and Experimental Study

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During the drilling of oil wells, drilling fluids are used to lubricate the drill bit, maintain hydrostatic pressure, transmit sensor readings, remove rock cuttings and inhibit swelling of reactive clay based shale formations. When water-based drilling fluids are employed, clay swelling can have a tremendously adverse impact on the drilling operation, significantly increasing well construction costs. The development of effective swelling inhibitor compounds does, and will continue to, attract, a large amount of interest.

Effective and more environmentally acceptable swelling inhibition may typically be achieved in water-based drilling fluids through the use of chemicals which incorporate appropriate

functionality that will interact favourably with the clay/shale interface. For example, for effective inhibition of clay swelling, low molecular weight polymers with localized hydrophobic and hydrophilic regions along the chain are typically used. On intercalation of these molecules within clay layers, the hydrophobic regions discourage further ingress of water, while the hydrophilic regions are believed to enhance the binding of highly hydratable sodium cations to the clay, preventing their hydration [1].

We report on the findings of a comprehensive programme of combined experimental techniques and high performance computer modeling work, undertaken to probe the mechanisms by which effective inhibition of clay swelling may be achieved. The focus of the investigations has been to correlate structural features of the inhibitor molecules with their efficiency in preventing swelling of a bentonite clay. Specifically, for a range of low to intermediate molar mass amine-functionalized poly(alkyleneglycol) ether polymers, the influence of backbone hydrophobicity, molar mass and number and orientation of the amine substituent's have been determined. Experimental techniques were chosen to explore the swelling inhibition process on the macroscale through to the microscale. Computational methods run in parallel to the experimental techniques have revealed information regarding the specific molecular interactions of the inhibitor and the clay.

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Selection of Demulsifiers for Electrocoalescence Dehydration

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Effective separation of crude oil and water appears as an essential operation to provide a dehydrated crude oil as well as a high quality water phase especially in the case of heavy and extra-heavy oils for which separation operations are becoming more and more difficult and costly. For instance, the separation process for bitumen extra heavy oils produced by thermal methods requires solvent addition, large concentration of chemical demulsifiers, high operating temperature as well as long residence times inside separation vessels.

In order to optimize the dehydration process in these difficult cases, electro coalescence may be used to favour water droplets coalescence and facilitate the separation of water. In this objective, a methodology was developed in order to select chemical demulsifier formulations specifically dedicated to the dehydration of stable water-in-crude oil emulsions by electrostatic processes. It is mainly based on the use of the electrical stability tester apparatus initially developed for oil-based drilling mud stability control (API 13B-2). The tests performed on reconstituted water-in-crude oil emulsions allow to follow the decrease of the critical voltage

recorded at a fixed intensity which corresponds to the short-circuiting condition of the apparatus. The higher the critical voltage value, the higher the stability of the emulsion. The test is then completed by the recording of the separation of water from the emulsion after the application of the electrical stress. So it is possible to select the best additive at an optimum concentration. The interpretation of the results issued from these tests may also give interesting information about the mechanism of action of the chemical demulsifiers (flocculation or coalescence). Finally, the validation of the efficiency of the selected concentration of additive is performed in an electrocoalescer device able to work at different frequencies and voltages.
