PETROLEUM RESEARCH JOURNAL

Environmental Friendly Electrochemistry – a Solution for a Clean Oil Industry .....
Petru Ilea 1

Nitrate for Corrosion Control, Souring Control and Improved Oil Production Braden Dunsmore and Giles Davis .....
Braden Dunsmore and Giles Davis 7

Fluid Selection Using Formation Damage Laboratory Testing - Key Parameters, Pitfalls and Potential .....
Ian Patey and Michael Byrne 13

The Methodology for Selection of Corrosion Inhibitors for Oil and Gas Applications
Ian George Winning and Derek McNaughtan 25

Development of a Bullhead RPM Water Control Treatment from Laboratory to Field .....
Mike Singleton, Dick Weare, Ken Sorbie and Robin Shields 35

Role of Steel Surface Finish on the Performance of Sodium Nitrite Inhibitor .....
Tala Abohalguma, F. El shawesh, Naiema Elahresh and W .BinZiglam 43

Overview of Scale Treatment in Oilfield Environments from a Technical Viewpoint
James A. McRae, Catherine J. Strachan and Alex Thornton 47

Scale Inhibitor Evaluation and Optimization .....
Salem Abuoun, Said Alforjani, Radia Sola , and Miloud Alarabi 55

Microbial Prevention of Wax Deposition During Transportation and Production of Crude Oil .....
Asma Attomi, I.EL Musrati, B. EL Gammoudi and M. EL Behlil 59

Evaluation of Imidazoline-based Inhibitors for Oil Environment by Means of Advanced Eelectrochemical Methods .....
G. Gusmano, G. Montesperelli, P. Labella, A. Privitera and S. Tassinari 67

Integrated Methodology for Mineral Scale Inhibitor Squeeze Treatments .....
B. Bazin, N. Kohler and A. Zaitoun 73

Demulsifying Power of Salts of Sulfated Ethoxylatated Nonylphenol and Their Combination with Certain Petroleum Sulfonates .....
Imad H. AL- Wahaib, Mahmoud F. Farhat and A.A. Obeid 81

VOLUME 17 - (2005)

Petroleum Research Centre
P.O. Box 6431, Tripoli
Great Socialist People's Libyan Arab Jamahiriya

Petroleum Res. J. Vol. 17 (2005): P. 1–6.

Environmental Friendly Electrochemistry – a Solution for a Clean Oil Industry

Petru Ilea*

الكيمياء الكهربائية الصديقة للبيئة- حل لصناعة نفطية نظيفة

بترو الي

تطورت أنظمة المعالجات الفيزيائية والكيميائية والحيوية التقليدية لكي تمنع التلوث وتحافظ على سلامة البيئة البشرية، وتبرز استخدام المعالجة الكهروكيميائية بديلا جذابا لهذه الأنظمة لمقاومة التلوث.

تعتبر الطريقة الكهروكيميائية التقنية نظيفة وأنيقة لأن الالكترونات الناتجة تمدنا على الأقل من هذه الناحية بكواشف متنوعة تستخدم للعديد من تفاعلات الأكسدة والاختزال ، ومن أجل ذلك فان تصميم مفاعل كهروكيميائي يتضمن أقطاب مصنوعة من مواد مناسبة وباستعمال وسائل تحكم هندسي للتفاعل يمكن أن يوفر حلا في الوقت المناسب لتجنب ملوثات محددة ناتجة من تحضير المركبات الكيميائية أو من إعادة استخدام الكواشف أو معالجة المياة أو مراقبة المواد السمية.

تعتبر المركبات العضوية السبب الرئيس لتلوث البيئة في صناعة النفط ، كما تعتبر المعالجة الكهروكيميائية أو تفكيك المركبات العضوية طرقا فعالة للتحكم في التلوث عند درجات حرارة منخفضة كبديل عن المحارق اذ تستطيع العمليات الكهروكيميائية التفكيك الكامل للمركبات العضوية وذلك بأكسدتها عن طريق المهبط أو اختزالها بواسطة المصعد الى مركبات عضوية صغيرة غير ملوثة . ويمكن أيضا بواسطة هذه الطريقة تفكيك الملوثات مباشرة خلال ما يسمى بالتحليل الكهربي وذلك عن طريق تفاعل الالكترونات المنقولة من والى الملوث التي تحدث على سطح القطب الكهربائي. ومن ناحية أخرى يمكن تفكيك الملوثات باستخدام عامل مختزل/مؤكسد مذاب (مثل $H_2O_2, O_3, HClO, Cl_2$) ناتج أو متضمن في المادة الالكتروليتية للتخلص من المادة الملوثة ، كما تتضمن هذه الورقة سلوك بعض العمليات الكهروكيميائية البيئية.

Abstract: *Conventional physical, chemical and biological treatment processes have been developed in order to prevent environmental pollution and to preserve the quality of human habitats. An attractive alternative for these processes are offered by the electrochemical approach of pollutant neutralization. Electrochemical processing is an elegant and clean technology because "electrons", at least from this point of view, may provide a versatile reagent for many redox reactions. Therefore, electrochemical reactor design, incorporating suitable electrode materials and using controlled reaction engineering, can provide a timely solution to avoid certain pollutants via clean synthesis, reagent recycling, water treatment or monitoring of toxic species.*

Organic compounds are the main cause of environment pollution in oil industry. The electrochemical treatment or destruction of organic compounds is potentially a powerful method of pollution control, offering a low temperature alternative to incineration. Electrochemical processes can determine the complete destruction of organic species by anode oxidation to carbon dioxide or cathode reduction to low or non-pollutant organic compounds. The electrochemical destruction of pollutants can be achieved directly through the so called direct electrolysis in which an electron transfer reaction

*"Babes-Bolyai" University, Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, Romania.

to or from the undesired pollutant occurs at the surface of an electrode. On the other hand, with the so called indirect electrolysis, the destruction of pollutants can be achieved with the use of a dissolved redox reagent (e.g. H_2O_2, O_3, $HOCl, Cl_2$ existing in or being generated from the electrolyte in order to neutralize the undesired pollutant. Some performance parameters of environmental electrochemical processes are also presented.

INTRODUCTION

Environmental pollution has become a considerable problem due to a rapid increase in the global industrialisation. In this context, the continuous rising demand of oil products has brought a rise in the crude oil extraction and processing. This fact has determined the appearance of important related environmental pollution problems.

The extraction leads to crude oil pollution of soil, natural waters and air in those areas. The crude oil components that pollute the environment, especially the soil, are accumulated and inflict negative consequences upon the flora and the fauna in the region. The human population also has a lot to suffer.

The main environment pollutants that originate from the extraction and processing of crude oil are presented in Table 1. As it can be seen, there is a great diversity of substances which will determine specific removal methods. Thus, conventional physical, chemical and biological treatment processes have been developed in order to prevent environmental pollution and to preserve the quality of the environment.

Table 1. Types of environmental pollutants from oil industry (after Sadiq[1], Kalabokas[2], and Obiajunwa[3]).

Organic pollutants	Inorganic pollutants
Alkanes Aromatic hydrocarbons Phenols Ketones Halogenated hydrocarbons Nitrated hydrocarbons Sulfonated hydrocarbons	Heavy and transitional metals NO_x, SO_x

Conventional chemical treatment processes are based on the usage of reagents. The products of their reaction often pose recycling problems or even pollution problems on a smaller scale than the original problem. Biochemical treatment processes are used very often but in certain situations, the high toxicity of the waste blocks the activity of the used biological species. An attractive alternative to the conventional treatment processes, which gain more and more interest, is electrochemical treatment. Electrochemical methods are of great diversity which can deal with a large number of pollutants related to the extraction and processing of crude oil.

This paper is an overview on electrochemical applications with regard to pollution problems in the oil industry. Research results obtained in the "Babes-Bolyai" University, Laboratory of Electrochemical Researches, Cluj-Napoca (Romania) on the in-situ electrosynthesis of hydrogen peroxide by cathodic reduction of dissolved oxygen in alkaline solution are mentioned.

GENERAL THEORETICAL ASPECTS ON ENVIRONMENTAL ELECTROCHEMICAL PROCESSES

Electrolysis for the production of useful chemicals and materials, energy producing electrochemical reactions and electrochemical methods for destruction of toxic or hazardous materials are environmental - friendly processes.

Electrochemical Technologies (ET) have definite advantages over the traditionally used physical or chemical processes. The inherent advantage of ET is the environmental compatibility, due to the fact that the main reagent, the electron, is a "clean reagent". The removal of pollutant species by oxidation/ reduction processes can be carried out directly in an electrochemical cell without the addition of redox chemicals. The high selectivity of many of these processes helps to prevent the production of unused by-products, which in some cases have to be treated as wastes. Other advantages of ET are (Rajeshwar[4], Juttner[5]): versatility (i) – direct or indirect oxidation and reduction, phase separation, concentration or dilution, ET can deal with a variety of pollutants, *e.g.* gases, liquids, and solids, and can treat small volumes of microlitres as well as large volumes of millions of litres; energy efficiency (ii) – ET generally have lower temperature requirements than their equivalent non-electrochemical methods *e.g.* thermal incineration; processes are easily monitored and automated via electrical signals (iii) and cost effectiveness (iv) electrochemical reactor and peripheral equipment are generally simple and, if properly designed, also inexpensive.

Considering electrochemical measures regarding

environment protection, three alternative concepts must be pointed out:

(i) Electrochemical processes for treating wastes- this includes all techniques where toxic compounds are removed from gases, liquids or even solids;
(ii) Process-integrated environmental protection – these include recycling of valuable material and substitution of waste-producing processes by cleaner ET with little or no waste production;
(iii) Electrochemical methods for environment monitoring, which will not be discussed here.

The main purposes of the environmental electrochemistry can be illustrated by considering examples from the following areas:

(a) Metal ion removal and recovery (*e.g.* Pt, Au, Ag, Cu, Sn, Zn, Ni, Cd, Hg).
(b) Regeneration of redox reagents (*e.g.* Cr (VI), Ce (IV), Ti (III), Fe (III) Ag (II)).
(c) Purification of water via disinfection using Cl_2, OCl^-, H_2O_2, O_3, OH^*.
(d) Concentration and separation of streams via membrane processes such as electrodialysis, electrochemical ion exchange.
(e) Sensing and monitoring of species via ion selective electrodes, gas sensors, microelectrodes.
(f) Removal of noxious gases, such as H_2S, SO_x, NO_x.
(g) Degradation and destruction of organic compounds such as phenols, chlorinated hydrocarbons, cyanides.

The basic parameters for an electrochemical process in the removal of impurities, but generally also for ET, are the current density, i – current per unit electrode area, the current efficiency, ϕ, and the space-time yield. The rate of an electrode reaction per unit of time is given by Faraday's law of electrolysis:

$$m = \frac{\phi\, i\, A}{z\, F} \quad [\text{mol s}^{-1}]$$

where A is the electrode area, z number of electrons and F is the Faraday constant. The current efficiency ϕ represents the ratio between the theoretical value of the current quantity given by Faraday's law and the real current quantity which is higher than the former due to possible secondary electrode reactions. The rate per unit reactor volume, V_R is:

$$\frac{1}{V_R}\cdot\frac{dm}{dt} = \frac{\phi\, i\, A}{z\, F\, V_R} \quad [\text{mol s}^{-1}\ \text{m}^{-3}]$$

which is the space-time yield.

The effectiveness of electrolysis for dilute solutions is strongly determined by the mass transfer of the species to be removed, the electrode surface area and the occurrence of electrode site reactions.

The current density represents the actual rate of an electrode reaction. Its maximum value, called the limiting current density, i_L, is defined by the following expression:

$$i_L = zFk_m c,$$

where k_m represents the mass transfer coefficient and c represents the bulk concentration of the species reacting at the electrode (the species which needs to be removed). In order to increase the value of the limiting current, two alternatives must be considered. Firstly, the mass transfer must be improved in order to have a higher value for k_m. This can be achieved by setting the electrodes in motion or by increasing the flow rate of the electrolyte solution. Secondly, the electrode area must be increased. To accommodate this, electrodes with a large active specific area are needed. Different types of electrodes with a large specific area are employed nowadays (*e.g.* porous electrodes, packed-bed electrodes, moving-bed electrodes). These electrodes are generally called three-dimensional electrodes and have a specific area ranging from 10^3 to 10^4 m^2/m^3.

ANODIC TREATMENT OF AQUEOUS EFFLUENTS AND ORGANIC WASTE

A partial or complete decomposition of pollutants can be achieved by anodic treatment. The organic material can be completely decomposed to carbon dioxide.

The decomposition of waste through anodic oxidation can be achieved directly on the anode surface or, indirectly, using appropriate anodically formed oxidants (*e.g.* Cl_2, hypochlorite, peroxide, ozone, Fenton's reagent, Cr^{6+}, Ag^{2+}).

Direct electrochemical oxidation methods are industrially of very little or no interest (Janssen[6]). The reasons for this are: (i) the rate of the electrochemical process is very small, (ii) the available electrode material is not inert (*e.g.* Pb corrodes slowly) and is expensive (*e.g.* borium-dopped diamond electrodes are very inert, but expensive).

Using chlorine-based compounds (anodically generated) as oxidation reagents are not

recommended due to a high risk of forming chlorinated organic compounds.

Oxidants like hydrogen peroxide and ozone can be used in open-end circuits because an excess of these compounds can be easily destroyed. These oxidants can be produced either on-site in special electrochemical cells (see below) or directly in the process liquids.

In order to obtain high efficiencies in the indirect oxidation process there are a few important requirements (Rajeshwar [4]). The potential at which the intermediate species is produced must be far from the value of oxygen generation. Next, the generation rate of the intermediate species must be large. Also, the reaction rate of the intermediate species with the pollutant must be higher than the rate of any competing reactions. Finally, the adsorption of the pollutant (or any other species) must be minimized.

Many anodic O-transfer processes occur with considerable overvoltage in the potential region for the anodic production of oxygen. The rate of the O-transfer process has been maximized without excessive oxygen evolution through the development of a doped metal oxide electrode material (e.g. Bi(V) doped – PbO_2).

Fenton's reagent, Cr^{6+}, Ag^{2+} and other such oxidants must be used in closed liquid circuits of the process in order to prevent metal losses.

Fenton's reagent is produced by the simultaneous cathodic reduction of Fe^{3+} and O_2 and subsequent reaction to the hydroxide radicals (Scott[7], Saracoo[8]):

$$O_2 + 2H^+ + 2e^- = H_2O_2$$
$$Fe^{3+} + e^- = Fe^{2+}$$
$$Fe^{2+} + H_2O_2 = Fe^{3+} + HO^- + HO^*$$
$$Fe^{2+} + HO^- = Fe^{3+} + HO^*$$

This species are very efficient in the oxidation of polycyclic aromatics, tarry and oily wastes, chlorinated aromatics and so on.

For a total oxidation only redox couples with high oxidation potential are suitable (*e.g.* Co^{3+} / Co^{2+} +1.82 V / NHE and especially Ag^{2+} / Ag^+ +1.98 V / NHE). Ag^{2+} is generated at the anode from Ag^+ in an aqueous nitric solution using an electrochemical cell divided by a membrane.

Phenols are considered one of the primary pollutant components in waste water due to their high toxicity (the limit for phenol concentration in water is 0.05 mg dm^{-3} and lower concentration limits are in discussion (Comninellis [9])), high oxygen demand (theoretically, 2.4 mg O_2 mg^{-1} phenol) and low biodegradability (Bahadir [10]).

Petrochemical refineries are one of the main sources of phenol pollution. In the past years, numerous treatment technologies have been proposed for phenol removal from wastewater (*e.g.* Comninellis[9]), Bahadir[10]). Thus, under suitable circumstances and in concentrations above 2-4 g/L, phenols can be economically recovered from waste waters (Canizares[11]). Below these concentrations, phenol destruction is always the best method for treating phenolic wastes. Among the existing processes, photochemical degradation, chemical oxidation, wet oxidation and electrochemical direct or indirect oxidations are of interest.

The direct anodic oxidation is characterised by a low reaction rate or low current efficiency. Phenol is well known for its ability to foul electrodes and the tarry deposit forming on electrodes during phenol oxidation is attributed to phenol polymerization products (Zareie [12]). Due to these circumstances, the indirect electrochemical oxidation, using redox couples with high oxidation potential, is the more preferable path.

CATHODIC TREATMENT OF AQUEOUS EFFLUENTS AND ORGANIC WASTE

The most important application of cathodic treatment is the removal of toxic metal ions from waste-water and organic waste. There is a considerable number of papers and some reviews in the literature referring to this topic (Rajeshwar [4], Jüttner [5], Janssen [6]). Also, most of the industrial applications are of this particular nature.

The recovery of metals from aqueous effluents by electrodeposition depends on the ion concentrations in the wastewater. If metal ion concentrations in the feed-solution are in the range of 1-3 g/dm^3 then two-dimensional cathodes should be used in order to achieve concentration levels of 0.1 – 0.5 g/dm^3 at the outlet (Scott [7]). Thus, the removal of a metal ion from a process stream to a pre-determined concentration enables the recycling of either solution or metal to be processed. If concentration levels of 0.001 g/dm^3 in the effluent are required, in order to process a feed solution with concentrations levels of 0.1 g/dm^3 of metal ions, three-dimensional electrodes are preferably used.

Our research was focused on the Cu removal from waste water and Cr^{6+} regeneration (Ilea [13, 14]).

The electrochemical reactor can operate continuously or in a batch mode and can produce either compact metal for re-use, powdered or flake metal, or concentrates for recycling.

Chlorinated organic compounds comprise another important category of substances that are amenable to cathodic reduction (Rajeshwar [4], Sequeira [15], Scott [7] , Rajeshwar [16]). These compounds can be reduced in acidic or basic solutions by a replacement mechanism to yield the less toxic aromatic parent compounds plus chloride ions.

Hydrogen peroxide can also be electrosynthesised by cathodic reduction of oxygen and used for the removal of low concentrations of organics. Also, hydrogen peroxide is a much more attractive mediator since the reactant can be oxygen from the air and any excess hydrogen peroxide eventually decomposes only to oxygen and water, therefore leaving no residual chemicals in the environment (Alvares-Gallegos [17]). However, in order to electrogenerate hydrogen peroxide directly in the wastewater, it is necessary to reduce the oxygen to hydrogen peroxide under quite different conditions in comparison with those used in commercial manufacturing processes.

The synthesize of hydrogen peroxide by partial reduction of oxygen has been carried out in alkaline media (Ilea [18, 19], Rosca [20]). The main advantage of this electrosynthesis is the low energy consumption because the reaction:

$$O_2 + H_2O + 2e^- \Leftrightarrow HO_2^- + HO^- \qquad \varepsilon^0 = -0.065V$$

(Kinoshita [21])

can be conducted at low cathodic polarisation.

The hydrogen peroxide electrosynthesis (HPE) was studied using classic linear voltammetry and wall-jet ring disk electrode techniques. The specific parameters of HPE were determined. Thus, the quasi-reversible character of the process, the average number of electrons transferred in the electroreduction of oxygen at carbonaceus materials electrodes, the current efficiency of HPE and the heterogeneous rate constant were established.

CONCLUSIONS

Electrochemical technologies can and will contribute to environment protection by means of waste purification processes. Some of these methods have been presented and briefly discussed here. Methods like the recovery of metals from aqueous effluents by electrodeposition are already frequently used, while other electrochemical techniques (*e.g.* direct and indirect anodic incineration of pollutants) are in competition with classic procedures.

Electrochemical methods can deal with a large number of pollutants related to the extraction and processing of crude oil. The possibility of using these methods on a large scale in the near future is related to the availability of some effective electrode materials. It is also related to the fact that through electrochemical technologies the recovered substance may have a significant resale value or it might be internally recovered in the process.

ACKNOWLEDGEMENTS

The author wishes to thank Dorneanu S., Popescu I.C. and Ilea C.G. for their help, comments and constructive criticism.

REFERENCES

[1] Sadiq, M. and Alam, I., 1997. Metal concentrations in a shallow groundwater aquifer underneath a petrochemical complex. *Water Research*, **31**, 3089-3097.

[2] Kalabokas, P.D., Hatzianestis, J., Bartzis, J.G. and Papagiannakopoulos P., 2001. Atmospheric concentratons of saturated and aromatic hydrocarbons around a greek oil refinery. *Atmospheric Environment*, **35**, 2545-2555.

[3] Obiajunwa, E.I., Pelemo, D.A., Owolabi, S.A., Fasasi, M.K. and Johnson-Fatokun, F.O., 2002. Characterisation of heavy metal pollutions of soils and sediments around acrude-oil production terminal using EDXRF. *Nuclear Instruments and Methods in Physics Research* B **194**, 61-64.

[4] Rajeshwar, K., Ibanez J.G. and Swain, G.M., 1994. Electrochemistry and the environment. *J. Appl. Electrochem.* **24**, 1077-1091.

[5] Jüttner, K., Galla U. and Schmieder H., 2000. Electrochemical approaches to environmental problems in the process industry, *Electrochimica Acta*, **45**, 2575-2594.

[6] Janssen, L.J.J. and Koene L., 2002. The role of electrochemistry and electrochemical technology in environmental protection. *Chemical Engineering Journal*, **85**, 137-146.

[7] Scott, K., 1995. Electrochemical processes for clean technology. *The Royal Society of Chemistry*, London, **175**.

[8] Saracco, G., Solarino L., Specchia V. and Maja, M., 1995. Electrolytic abatement of biorefractory organics by combining bulk and electrode oxidation processes *Chemical Engineering Science*. **56**, 1571-1578.

[9] Comninelis, C. and Pulgarin, C., 1991. Anodic oxidation of phenol for water waste treatment. *J. Appl. Electrochem.* **21**, 703-708.

[10] Körbahti, B.K. and Tanyolac, A., 2003. Continuous electrochemical treatment of phenolic waste water in a tubular reactor. *Water Research*, **37**, 1505-1514.

[11] Canizares, P., Dominguez, J.A., Rodrigo M.A., J. and Villasenr, J., and Rodriguez, J., 1999. Effect of the current intensity in the electrochemical oxidation of aqueous phenol wastes at an activated carbon and steel anode. *Ind. Eng. Chem. Res.*, **38**, 3779-3785.

[12] Zareie, M. H., Körbahti, B.K. and Tanyolac, A., 2001. Non-passivating polymeric structures in electrochemical conversion of phenol in the presence of NaCl. J. of *Hazardous Materials*, **B87**, 199-212.

[13] Ilea, P., Buda, C. and Dorneanu S.,1998. Electrochemical recovery of copper from synthetic electrolyte and industrial waste electrolyte. *Chem. Bull. "Politehnica"* Univ. Timisoara, **43**, 18-22.

[14] Ilea, P, Kolozsvari, K., Oniciu L. and Pop, R.,1996. The oxidation of Cr^{+3} to Cr^{+6} on different anodic materials. Cyclic voltammetry study, proceeding Abstr. P4a-7, The 47th Annual Meeting of the ISE, Veszpren-Balatonfured, Hungary.

[15] Sequeira, C.A.C., 1994. *Environmental Oriented Electrochemistry*, Elsevier, Amsterdam, 45.

[16] Rajeshwar, K. and Ibanez, J.G., 1997. *Environmental Electrochemistry – Fundamentals and Applications in Bollutiona Abatement.* Academic Press, San Diego, California, p.377.

[17] Alvarez_Gallegos, A. and Pletcher, D., 1999. The removal of low level organics via hydrogen peroxide formed in a reticulated vitreous carbon cathode cell. Part II. The removal of phenols and related compounds from aqueous effluents. *Electrochimica Acta*, **44**, 2483-2492.

[18] Ilea, P., Dorneanu, S. and Nicoara, A.,1999. Hydrogen peroxide electrosynthesis by partial oxygen reduction in alkaline media. I. Voltammetric study unmodified carbonaceus materials. *Revue Roumaine de Chimie*, **44**, 555-561.

[19] Ilea, P., Dorneanu S. and Popescu I. C., 2000. Hydrogen peroxide electrosynthesis by partial oxygen reduction in alkaline media. II. Wall-jet ring disk electrode for electroreduction of dissolved oxygen on graphite and glassy carbon. *J. Appl. Electrochem.*, **30**, 187-192.

[20] Rosca, V., Ilea P. and Popescu, I. C. 1999. Electrosynthesis of hydrogen peroxide by partial reduction of oxygen in alkaline media. Part III. Wall-jet ring electrode for hydrogen peroxide amperometric detection. *Stud. Univ. "Babes - Bolyai", Chem.*, **44**, 295-300.

[21] Kinoshita, K., 1992. *Electrochemical Oxygen Technology*. J. Wiley & ?Sons, New York, 32.

Petroleum Res. J. Vol. 17 (2005); P. 7–12, 1 Fig.

Nitrate for Corrosion Control, Souring Control and Improved Oil Production

Braden Dunsmore and Giles Davis*

استخدام النيترات للتحكم في التآكل والحمضية وتحسين إنتاج النفط

برادن دنسمور وجاليس ديفس

تعتبر أملاح النيترات رخيصة الثمن نسبيا وسهلة المناولة وصديقة للبيئة ، لذلك فقد استخدمت منذ زمن للتحكم في البكتيريا المختزلة للكبريتات (SRB) وفي معالجة مياه الصرف الصحي وتستخدم الآن على نطاق واسع في منظومات حقول النفط.

لقد تم في هذه الورقة مناقشة الآليات المختلفة التي تعمل النيترات بواسطتها للتخفيض من كثافة تجمعات البكتيريا المختزلة للكبريتات والمسببة للتآكل ورفع حموضة المكامن الناتجة عن الكبريتيد المفرز كإنتاج جانبي. ولقد تم التدليل على أن النيترات تستطيع تخفيض التآكل والحموضة الناتجة عن تكون البكتيريا المختزلة للكبريتات في المختبر وفي الحقل، وإضافة إلى ذلك فان النيترات لها قدرة تحفيز تكون البكتيريا الحميدة المانعة لتكون البكتيريا المختزلة للكبريتات، ومن ثم تحسين استرداد النفط المتبقي بالمكامن.

Abstract: *Nitrate salts are relatively cheap, easy to handle and environmentally friendly. They have historically been used to control sulphate-reducing bacteria (SRB) problems in the municipal waste-water industry and are now becoming widely used in oil field systems. Nitrate acts via numerous mechanisms, which are discussed, to reduce the population of SRB in a system. SRB are responsible for microbiologically influenced corrosion (MIC) and souring of reservoirs by the sulphide by-product, which they excrete. Evidence is presented to show that nitrate can reduce corrosion and souring by SRB in the laboratory and also in the field. In addition, nitrate can also stimulate useful bacteria, which can prevent the return of SRB and also improve residual oil recovery from reservoirs.*

INTRODUCTION

Oilfield microorganisms have been shown to originate in the subsurface and to enter wells, along with substrates that may enhance their growth, upon water injection for secondary oil recovery. Sulphate in the injected water, e.g. seawater, provides the electron acceptor to allow growth on the organic nutrients present in formation water (Bass and Lappin-Scott [1]). In many oilfields this gives rise to a dominant population of sulphate-reducing bacteria (SRB). SRB are responsible for problems such as souring (contamination) of crude oil with sulphide, a respiratory by-product (Ligthelm *et al.* [2]; Sunde *et al.* [3]). In addition, SRB can enhance corrosion of pipelines and process equipment while biofilm growth can block porous rock near to injection well bores (Jack and Westlake [4]).

The oil industry has traditionally responded to microbial problems with chemical biocide treatments. However, biocides may persist in marine environments (Martinez *et al.* [5]), are often

* Oil Plus Ltd, United Kingdom.

ineffective (Boivin, [6]), and SRB have been shown to develop resistance to some biocides (Lui *et al.*[7]). The use of nitrate to alter the ecology of a sour oil field system was proposed by Jenneman *et al.* [8]. In the laboratory 22 mg/l nitrate ion addition was insufficient to reduce sulphide production but was able to maintain sulphide inhibition after previous treatment with 44 mg/l (Reinsel *et al.* [9]).

Nitrate and nitrite have been shown to reduce sulphide levels and SRB numbers in field trials at concentrations of less than 300 mg/l (Sturman and Winters [10]) and recent field experience in the North Sea has shown that nitrate at much lower concentrations is also successful. The various potential mechanisms, by which nitrate can act, are presented here. The advantages and disadvantages of using nitrate when compared to dosing conventional biocides are discussed, and some case histories from recent field use are also presented. Finally, advice on using nitrate in oil field situations is given.

HOW NITRATE WORKS

There are several mechanisms by which nitrate or nitrite may remediate souring and these are discussed below. However, it is first necessary to briefly discuss the relevant bacterial metabolic reactions in order to understand the principle of nitrate treatment. Essentially, anaerobic bacteria reduce compounds such as nitrate, nitrite or sulphate in the same way that animals respire oxygen. In combination with this, bacteria must also oxidise a suitable carbon source as food.

Sulphate reduction: Carbon source + $SO_4^{2-} \rightarrow CO_2 + H_2S$ + Energy
Carried out by sulphate-reducing bacteria (SRB)

Nitrate reduction: Carbon source + $NO_3^- \rightarrow CO_2 + NO_2^-$ + Energy
Carried out by nitrate-reducing bacteria (NRB)

Denitrification: Carbon source + $NO_3^- \rightarrow CO_2 + N_2$ + Energy
Carried out by denitrifying bacteria (DNB)

(NB: Importantly, nitrate reduction and denitrification produce more energy than sulphate reduction).

The possible mechanisms by which nitrate may control souring are:

Bacterial Competition:

Sulphide formation by SRB is prevented by NRB/DNB out-competing the SRB for the available carbon nutrients. They can out-compete the SRB because more energy is produced by respiring nitrate and so NRB/DNB will grow and reproduce faster than the SRB. This is often the major mechanism behind souring control with nitrate, hence use of nitrate may be described as a bio-competitive exclusion process.

Biological Oxidation:

Perhaps a secondary mechanism in most cases, the activity of nitrate-reducing, sulphide-oxidising bacteria (NRSOB) causes sulphide removal and sulphate production. The exact mechanism is unknown but potentially:

$$H_2S + NO_3^- \rightarrow NO_2^- \text{ (or } N_2\text{)} + SO_4^{2-} \text{ (or elemental S)}$$

Inhibition of SRB:

NRB inhibit SRB activity by production of nitrite, which is biocidal and increases the redox potential of the system away from the optimum redox for SRB activity. It has also been suggested that nitrite may scavenge sulphide to a degree.

$$NRB + NO_3^- \rightarrow \text{(possibly via NO / } N_2O) \rightarrow NO_2^- \text{ (or } NH_4^+)$$

Change of Electron Acceptor:

Some SRB are able to switch electron acceptor and may use nitrate in preference to sulphate if it is readily available. Hence they act as NRB, generating by-products such as nitrite and ammonium instead of sulphide.

It is likely that in the environment a combination of all the above factors leads to effective treatment of souring by nitrate application.

Hence, given the variety of possible mechanisms it is important to define the optimum NO_3^- concentration for any given situation.

WHY USE NITRATE ?

Advantages

The advantages of nitrate treatment over conventional biocides are numerous. Firstly, and most

importantly, nitrate offers a realistic option to treat a reservoir (biocides are more successful when used on topside equipment). Nitrate does prevent sulphide generation by bacteria but does not depend on killing SRB to be effective. This can be considered an advantage as biocide strategies rarely give a 100% kill of nuisance bacteria. Therefore, some bacteria will always be available to grow and divide to be a source of contamination to other areas of a system.

Nitrate is a cheaper chemical per litre than most biocides. Table 1 gives approximate comparative costs to some popular types of biocide. However, dosing may be roughly equivalent when overall costs are considered (see disadvantages below).

Table 1. Approximate costs of anti-microbial chemicals. Price per year based on dosing a 200,000 BWPD water injection system.

	Pric/litre (US$)	Dose regime (hypothetical)	Price/ year (US$)
Nitrate (50% Ca $(NO_3)_2$	0.25	60 continuous	575,000
THPS (50% solution)	4	500 for 1h 2xLweek	500,000
Glutaraldehyde (50% solution)	2.5	500 for 1h 2x/week	345,000
(* does not include transport/manpower). (Dose regimes in mg/l nitrate ion or mg/l biocide product).			

Nitrate is considerably less toxic than any biocides or H_2S scavengers in use. It is therefore, by definition, safer to handle and more environmentally friendly. It is classified as posing little or no risk to the environment (PLONOR) although there are some environmental effects, discussed below. By comparison glutaraldehyde and THPS are in HOCNS category C which means discharges in excess of 15 tonnes/ platform/year have to be notified to the authorities (in the UK).

Disadvantages

Despite the cheaper cost per litre, dosing nitrate is often carried out continuously. It is therefore more expensive overall because large volumes are needed to maintain the desired bacterial population. Higher transport costs also result, which can be a major factor when considering an offshore application. Further additional costs are related to increased manpower for dosing and monitoring.

Nitrate does not kill bacteria, and while this can be an advantage as discussed above it can also be considered a disadvantage depending on the situation. In some cases biomass of any kind is undesirable. A beneficial population of NRB may prevent sulphide generation but this biomass may risk formation damage in some cases. Nitrate is also a nutrient source for all types of bacteria and in a situation where it was previously limiting to growth its addition may stimulate damaging growth by bacterial types other than NRB.

Due to the complexities of nitrate dosing, to subtly alter the bacterial population, specialist advice is often required and more intensive monitoring needed. The results from such monitoring again may require interpretation by specialists.

Finally, proper control trials in operating oilfields are usually not possible and so results, which may take some time to show, can be difficult to prove. Yet such proof is often demanded at an early stage in order to continue trials and field dosing.

CASE HISTORIES FROM THE LABORATORY AND THE FIELD

Corrosion Control

Statoil has successfully used nitrate on the Veselfrikk field in the North Sea. From the onset of seawater injection in 1994 through to 1997, an increase in SRB and corrosion rates was measured. Nitrate was then applied, resulting in corrosion rates one third as great as pre-treatment rates. This was accompanied by the overall quantity of sessile bacterial biomass remaining constant. The theory behind the successful corrosion control by nitrate centres around disruption of the iron sulphide : mild steel galvanic corrosion cell which commonly forms when SRB biofilm creates and entrains iron sulphide.

Souring Control

A successful trial performed by Maersk Oil in the Skjold Field varied the concentration of nitrate, when applied as $NaNO_3$ from 87 – 270 mg/1 nitrate ion (Larsen[10]). However, these treatments required continuous addition of chemical and so for offshore applications logistics and related costs tend to limit the maximum applicable dose concentration. However, recently nitrate injection has been performed from day one on a new field development, which has so far resulted in delaying the onset of predicted souring. In this case dosing was performed

at a considerably lower rate, some 60 mg/l nitrate ion (Larsen[11]).

By contrast to these successful treatments Shell performed an unsuccessful field trial on North Cormorant where dosing at a maximum of 34 mg/l nitrate ion did not result in any detectable decrease in H_2S. The trial was not ideal however and the dose rate was as low as 17 mg/l nitrate ion during some periods (Frigo[12]).

Microbially Enhanced Oil Recovery (MEOR)

Non-deaerated seawater, nitrate and phosphate are currently being injected to Statoil's Norne field, which has apparently resulted in around 6% additional oil reserves (30 million barrels) being produced over the last year. This process also involves the injection of a special consortium of bacteria known to produce surfactants. These surfactants are produced *in situ* at the oil : water interface and are said to be many times more efficient than injection of chemical surfactant. Oil Plus and the UK DTI are planning joint industry research projects to investigate this potentially lucrative process.

HOW TO USE NITRATE SUCCESSFULLY

Pre-Trial Assessment

Before any decision to use nitrate in the field, a pre-trial assessment must be completed. Nitrate is not suitable for every situation and the applicability of any particular strategy must be assessed. Nitrate can be applied from day one of water injection (refer to the above section) and in many cases this may be the best time to begin treatment if the souring potential for a new development is high. In addition, the appropriate dose concentration should be determined to add maximum value at minimum cost. There is no recommended dose for all situations, it varies depending on carbon source availability in the reservoir among other things. Some simple field-testing can often help give an accurate assessment and provide a baseline from which to begin treatment. Recommended dose rates should be determined using a combination of field experience and laboratory studies. A simple example laboratory study shows how there is a distinct cut-off in efficiency of nitrate under certain conditions; in this case 62 mg/l is effective. (Fig. 1) - Please note that the carbon source for these tests was specific to a given situation and these

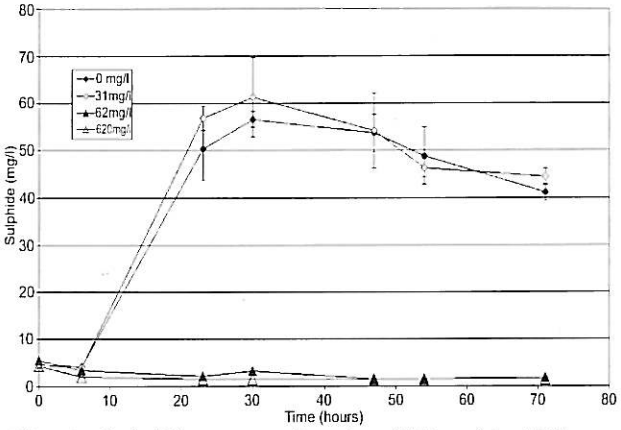


Fig. 1. Sulphide generation by SRB with different concentrations of nitrate (mg/l nitrate ion). Note: required nitrate concentrations vary widely depending on situation/ water/ carbon sources etc.

concentrations can vary dramatically for different fields.) Depending on the prevalent mechanisms in a particular field, a different concentration of nitrate may be needed. In addition, any nitrate treatment should be designed to complement existing anti-microbial measures, and the appropriate dosing point should be selected.

Field Trial

Comprehensive monitoring must be carried out, prior to and during a field trial. This is essential to evaluate the nitrate treatment in the field. Specialist advice will be needed and should be sought in order to ensure that the potential benefits of nitrate injection are realised. Monitoring should include tests for nitrate, nitrite and sulphide, as well as nitrate-reducing bacteria and nitrate-reducing, sulphide-oxidizing bacteria. In addition, molecular tools can be used to detect successful nitrate treatment: certain species of nitrate-utilizing bacteria have been associated with successful nitrate treatment. At this stage it is also crucial to optimize the nitrate dose rate.

Full Field Use

A monitoring system needs to be established to assess the long-term efficacy of any treatment. This routine testing should be set-up by a specialist consulting team, during the field trial, so that any necessary training and equipment can be handed over for correct continued monitoring by on-site staff. Periodic assessment of the data should then be made, perhaps with expert advice, to ensure that nitrate dosing is optimized, saving on unnecessary

expenditure, and that the nitrate treatment continues to have the desired effect. Comparison of nitrate use, versus biocide and H_2S scavenger expenditure can also be made to determine the benefit of using nitrate.

REFERENCES

[1] Bass, C. J. and Lappin-Scott, H. M., 1997. The bad guys and the good guys in petroleum microbiology. *Schlumberger Oilfield Rev.* **9**, 17-25.

[2] Ligthelm, D. J., de Boer, R. B., Brint, J. F. and Shulte, W. M., 1991. Reservoir souring: an analytical model for H_2S generation and transportation in an oil field reservoir owing to bacterial activity. **SPE** 23141. Proc. Offshore Europe Conf., Aberdeen, September 3-6, 369-456.

[3] Sunde, E., Thorstenson, T. Torsvik, T., Vaag, J. E. and Espedal, M. S., 1991. Field-related mathematical model to predict and reduce reservoir souring. **SPE** 25197. Proc. SPE International Symposium on Oilfield Chemistry, 449-456. New Orleans, March 2-5.

[4] Jack, T. R. and Westlake, D. W. S., 1995. *Control in Industrial Settings. Biotechnology Handbook 8:Sulphate-Reducing Bacteria. Barton,* L. L. (ed.) Plenum Press, New York. 265-292.

[5] Martinez, K., Ferrer, I., Hernando, M. D., Fernandez-Alba, A. R., Marce, R. M., Borrull, F. and Barcelo, D., 2001. Occurrence of antifouling biocides in the Spanish Mediterranean marine environment. *Environ Technol.* **22**, 543-552.

[6] Boivin, J., 1995. Oil industry biocides. *Mat Perf.*, **34**, 65-68.

[7] Lui, H. F., Xu, L. M., Zheng, J. S. and Liu, J., 2000. New bactericide for biocide resistant sulfate-reducing bacteria. *Mat Perf.* **39**, 52-55.

[8] Jenneman, G. E., McInerney, M. J. and Knapp, R. M., 1986. Effect of nitrate on biogenic sulphide production. *Appl Environ Microbiol.* **51**, 1205-1211.

[9] Reinsel, M. A., Sears, J. T., Stewart P. S., and McInerney, M. J., 1996. Control of microbial souring by nitrate, nitrite or gluteraldehyde injection in a sandstone column. *J. Ind Microbiol.* **17**, 128-136.

[10] Larsen, J., 2002. Use of nitrate for prevention of souring in the Skjold field. Proceedings from NACE Annual Conference. Denver.

[11] Larsen, J., 2003. Use of nitrate for prevention of souring in the Halfdan field. Proceedings from Reservoir Microbiology Forum (RMF) 9. London.

[12] Frigo, D., 2003. Shell experiences with nitrate. Proceedings from Reservoir Microbiology Forum (RMF) 9. London.

Petroleum Res. J. Vol. 17 (2005); P. 13–24, 8 Figs.

Fluid Selection Using Formation Damage Laboratory Testing - Key Parameters, Pitfalls and Potential

Ian Patey and Michael Byrne*

اختيار السوائل باستخدام معايرة معملية لتشوه التكاوين الجيولوجية أهم المتغيرات والمخاطر الكامنة والاحتمالات

ايان باتي وميخائيل بايرني

تتم اختبارات تشوه التكاوين بصفة متكررة لاختيار سوائل الحفر المناسبة قبل استخدامها بالآبار. وتعتمد القرارات الرئيسة التي تؤثر على إنتاجية وحقن الآبار على هذه الاختبارات ا لمعملية.

تصبو هذه الورقة لحل بعض من الجدل والاختلاف حول طرق اختبارات تشوه التكاوين وتقدم دليلا واضحا لدعم الآراء التي تم طرحها حول مميزات بعض من أنواع الاختبارات. وتصف هذه الورقة وبصورة مفصلة بعض الطرق التي يجب أن تؤخذ في الاعتبار أثناء إجراء أو طلب اختبار تشوه التكوين معمليا. كما تمت مناقشة الاختلافات في طرق الاختبار عند تحضير عينات لب البئر وعند محاكاة الإنتاج وقد عبر المؤلفان وبآراء واضحة على ما يعتقدانه أفضل الخيارات.

تم عرض أهم المشاكل التي تواجهه عملية تصميم التجارب المعملية وكذلك تقديم خطوط إرشادية مدعومة بأدلة واضحة باتجاه اختيار طرق معينة عن غيرها. كما تم تقديم أحدث التطورات عند تصميم الاختبار وتفسير نتائجه ونوقشت الاستعمالات الحالية والمتوقعة للنتائج المعملية، وقدم الباحثان آرائهما حول التقدم المحتمل واتجاهات البحث العلمي مستقبلا في هذا المجال الحساس.

خلصت المقالة إلى أن اختبار تشوه التكوين معمليا جدير بالمحاولة، ولكنه يتطلب تخطيطا وتصميما دقيقين. إن طرق الاختبارات المختلفة يجب أن يؤخذ بها بعناية حتى تكون النتائج قادرة على التنبؤ أو تعكس الواقع الفعلي لأداء البئر والمكمن.

Abstract. *Formation Damage laboratory testing is routinely performed to select optimum drilling, completion and other fluids prior to their deployment in wells. Major decisions which impact the productivity or injectivity of wells and fields are often based on laboratory tests. This paper aims to resolve some of the arguments and diversity in the procedures for laboratory formation damage tests and present clear evidence to support opinions expressed on the merits of particular tests.*

This paper describes in detail some of the procedures which need to be considered when conducting or ordering formation damage laboratory tests. From core preparation through to simulation of production, the differences between test methods are discussed and the authors express clear opinions on what they consider as the best approach.

Some of the biggest pitfalls which are encountered when designing laboratory tests are explained and guidelines are presented, backed by clear evidence which point towards particular methods and away from others.

The latest advances in test design and test result interpretation are presented. The current and potential use of laboratory data is discussed and the authors present their opinions on likely future

* Formation Damage Group, Corex UK Ltd. Scotland.

advances and the direction of future research in this critical area.

The paper concludes that laboratory formation damage testing is worthwhile but it must be carefully planned and designed. The various test methodologies must be carefully considered in order for the results to predict or reflect real well and reservoir performance.

INTRODUCTION

Over the past 18 years various laboratory projects have been designed and conducted by the authors to improve well productivity and injectivity by understanding and mitigating formation damage. One of the most important factors in design of laboratory testing for formation damage is to decide if the test objective is to compare fluids procedures or to attempt to simulate real well behavior or both. The majority of formation damage testing referred to in this paper should be viewed as a combination of simulation and comparative testing. Another critical factor in testing is that all tests are conducted at reservoir conditions in suitable equipment. All reservoir conditions wetted parts must be composed of corrosion resistant materials such as Hastelloy and Teflon. Testing in inferior quality equipment will be prone to artifacts and will generate erroneous results.

Samples for testing must be carefully selected and prepared in order to obtain results that are relevant for the reservoir under investigation. Laboratory testing, if performed carefully and with due consideration to sample selection and test design, can accurately measure potential reduction in permeability. In order to use this information and enhance productivity it is often necessary to determine the precise cause or causes of Formation Damage. Identifying damage and interpreting the results of advanced core flood tests usually requires a combination of engineering and geological skills. Geological techniques such as Scanning Electron Microscopy (SEM) and Thin Section analysis can be used to identify solid damaging mechanisms such as solids invasion, residual mud cakes, precipitates, fines migration or bacterial growth. Cryogenic SEM involves preparing part of the sample after the flood test down to liquid nitrogen temperature and analysis of this frozen specimen. This technique allows the identification of fluid damaging mechanisms such as wettability alteration, water blocks and micro-emulsion formation. By combining engineering and geological skills, it is not only possible to examine and simulate Formation Damage problems but diagnose those problems and help to prescribe the best treatment or the least damaging procedure.

One of the most important influences on Formation Damage is the geology of the reservoir. In order to apply the data produced from a laboratory test, it is essential to understand the relevance of the rock material tested. Samples for laboratory testing must be selected to represent the major production or injection intervals. If there are significant differences in permeability or clay type, for example, these differences must be adequately represented in the material for testing. All available geological and relevant production data should be used in order to select the most suitable core material. Samples preserved with reservoir fluids in the pore space are preferred but old, dried out core may be restored to very close to the reservoir conditions using careful handling techniques. Special cleaning and drying procedures should be employed to ensure that samples selected are prepared without altering delicate structures in the pore space. The laboratory tests are designed to incorporate all pressure changes in the near wellbore area. For example, if the well under investigation is to be returned to production by gradually decreasing the pressure in the wellbore (drawdown), then this-step should be incorporated in the laboratory test.

As technological advances are made and environmental concerns increase, new challenges confront those involved in dealing with Formation Damage problems. New environmentally friendly drilling fluids may not be particularly reservoir friendly, and need to be carefully selected for each application. Extended reach drilling can often lead to increased Formation Damage problems that can be expensive or impossible to remove. High temperature reservoirs may be damaged by breakdown of normal fluids under the intense conditions. H_2S production from microbial activity may cause problems that need to be minimized with environmentally friendly solutions. New sand control completion techniques should be thoroughly assessed for their impact on productivity. Old or marginal fields may benefit enormously from a reassessment of historical Formation Damage that can now be avoided. The list goes on but the key to resolving all of these problems is thorough laboratory simulation combined with full sample evaluation to identify problems and solutions.

Laboratory testing cannot recover all of these

losses caused by Formation Damage but it can go a long way towards recovering significant amounts. By definition, properly constructed tests increase our understanding of the performance of each reservoir and can make a real difference to production, injection and profit.

Previous papers have suggested at the relative values obtained from one laboratory to another for the same tests can vary significantly[1,2]. This paper aims to dispel some of the misconceptions which surround laboratory testing and stimulate discussion and thought about the design, implementation and use of future laboratory tests. Based on collective authors' experience of more than 1,500 reservoir specific laboratory core flood tests some of the key parameters will be discussed and a recommended approach will be outlined. Potential pitfalls and errors during testing, some alluded to in previous publications will be presented and discussed. Evidence of the effects of corrosion in poor quality equipment, damage to samples prior to testing and the induced damage that can be measured due to poor laboratory procedures will be presented for the first time.

The case for particular laboratory test procedures will be made with the objective of increasing the reliability and relevance of laboratory formation damage testing. With an elevation of standards and thorough interpretation, laboratory testing can increasingly be used to predict and optimize well performance.

Finally the way forward for laboratory testing and the potential improved use of results obtained will be explored.

KEY PARAMETERS AND PITFALLS

The tests should be viewed as laboratory simulations. The criteria for test selection are therefore dependent on the well or field information to be simulated. Some of the basic categories are as follows:

Sample Selection

It is critical to select appropriate samples for all reservoir specific formation damage testing. In the tests, the objective is to simulate a reservoir or a well. If there are several different lithologies or rock types which contribute to production or will take injection, then all of these variations must be represented. If there are significant variations in permeability or lithology then additional samples will be required to represent the reservoir. Of course, the number of samples selected is a financial as well as scientific choice. Each additional lithology will increase the number of tests required and the cost of any project. Core samples from the well being studied or from adjacent or equivalent wells must be selected, the first selection criteria is that the core samples are representative. Then, the samples must be "in a good condition". In a good condition means that it is possible to obtain core plug samples which are representative of the key lithologies. Preserved samples have the advantage that the core is complete and it is therefore possible to take more or longer plug samples. Preserved samples may also have the advantage that the pore fluids are still in place and they do not require cleaning and restoration. Experience has shown us that many preserved samples have desaturated to some extent and so must be cleaned and restored. As illustrated in Figure 1, some preserved samples are contaminated with bacteria and should not be used. Normally, many plug samples are taken and prepared for testing. Sub-selection of samples is then performed to ensure that duplicates are used for the flood tests.



Fig. 1. Microbial contamination of preserved sample. A rock chip from a preserved sample which has been immersed in solvent. A stream of biopolymer can be seen eluting from the pore space. This sample was ruled unsuitable for formation damage testing due to bacterial contamination.

Core Preparation

Computer Axial Tomography (CAT) Scanning of the whole core samples is performed in order to determine correct orientation and selection of plugging sites for duplicate core plug samples. Samples are usually taken parallel to principal flow direction in

reservoir *i.e.* horizontal core plugs cut parallel to bedding. Either 1.5 or 1 inch diameter samples are used and length is limited to approximately 2 inches due to constraints of ultracentrifuge. Core plug samples should be cut using an inert mineral oil as bit lubricant to avoid damage.

Cleaning and Drying

The majority of reservoir rock samples available for testing are either poorly preserved or not preserved. To proceed for testing, they need to be cleaned of residual solids and fluids. There are many different methods for cleaning samples and the selection of the optimum method can have a profound effect on all results obtained from subsequent tests.

One popular method for cleaning is to flow fluids or combinations of fluids through the plug samples in a core holder. Amongst the potential problems with this method are: potential for fines migration to occur prior to the real laboratory testing; poor cleaning efficiency-inefficient sweep of all pores; difficulty in achieving required saturation with subsequent fluids.

Hot soxhlet solvent extraction can also be used to rapidly clean samples. This technique is now largely discredited due to severe alteration to delicate minerals which can occur. The photographs presented in Figures 2 and 3 are adequate evidence to condemn this technique where important decisions are made on the basis of the core flood testing.

We believe that the best methods for cleaning of samples are cold static cleaning and warm constant immersion cleaning. Cold static cleaning is normally prohibitively time consuming but warm constant immersion achieves good results in reasonable time

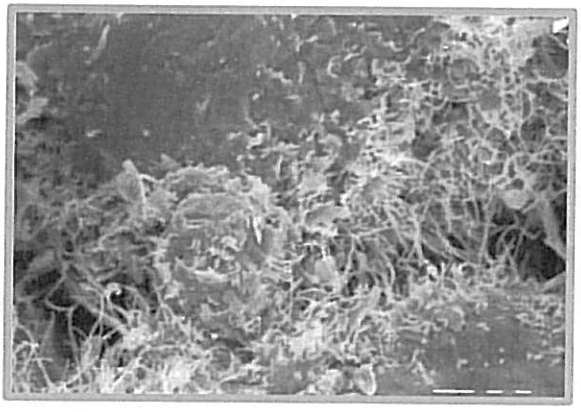


Fig. 2. Sample preparation - successful. The SEM photograph shows a pore in a sandstone reservoir filled with delicate illite fibres. Continuous immersion soxhlet cleaning and careful drying has preserved delicate structures maintaining the sample in a suitable state for core flood testing.

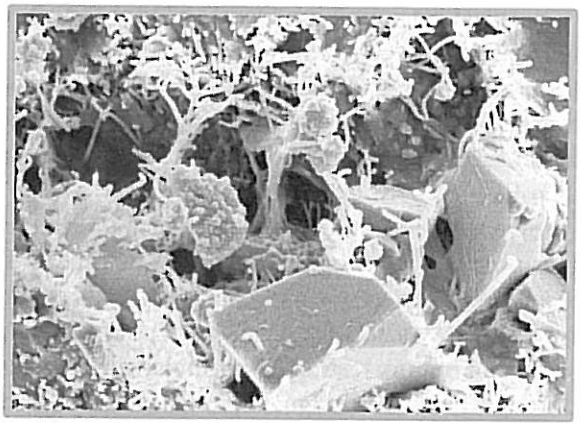


Fig. 3. Sample preparation – failed. As a contrast of figure 2, this sample from an identical continuous rock sample shows severe destruction of natural illite clay. The aggressive cleaning and drying used has destroyed the delicate illite fibres and rendered the sample unsuitable for core flood testing.

Samples are dried by low temperature oven drying to retain the intrinsic structures within the pore space.

Preparation to Fluid Saturation

For oil or gas leg simulation, the sample is saturated 100% to the formation water (pH adjusted), then prepared to irreducible formation water saturation using production phase (to eliminate relative permeability effects). Normally, this preparation to irreducible is achieved using an ultracentrifuge. There are three options-1 Ultracentrifuge, 2 dynamic (flooding), 3 porous plate. Ultracentrifuge rapidly achieves an irreducible saturation which is repeatable and consistent. Drawbacks such as variable saturation profile are outweighed by the benefits of this method and so it is the preferred technique for suitable core.

Dynamic flooding is the best option for samples which cannot withstand the physical forces of the ultracentrifuge. The technique suffers from incomplete sweep and from the fact that the flowing phases can induce fine migration. The porous plate is reliable and produces a consistent saturation profile but in most cases it is prohibitively slow and there can be contact material artifacts introduced to the plug sample.

Test fluids

It is the properties of reservoir fluids in the near wellbore that dictate the test fluids. For production wells, gas and oil are the most common test fluids. Convention is to use inert humidified nitrogen gas to represent producing gas phase. The majority of damage mechanisms are not dependent on the use

of live gas in the tests. For oil wells, convention is to use dead crude oil to represent producing oil phase. Tests with live crude oil can be conducted but are generally considered to be prohibitively expensive. Experience with dead crude oil has led to the development of special laboratory procedures which are important to observe in order to avoid artifacts. The oil must be completely dewatered and must be maintained at all times above the wax appearance temperature. The oil must be filtered at reservoir conditions to very fine specifications to avoid introducing particles to the test. If insufficient crude oil is available (approximately five liters for each test) or if the crude oil is unstable (*e.g.* due to asphaltene deposition), inert mineral oil of similar viscosity to the crude oil can be substituted.

The appropriate fluid phase should be used for any simulation. Oil should not be used to represent gas as the relative clean-up of any damage with oil and gas may differ.

Flow Direction

The direction of flow of fluids through a core plug sample during testing should reflect real wellbore flow directions at all times. Terms such as "forward, reverse, inlet, outlet, upstream and downstream" should not be used during formation damage simulations for production or injection wells. These can lead to confusion in test procedures and interpretation. For example, during simulation of drilling a water injection well, the permeability we are most interested in is from the well to the reservoir with injection water. This could be described as forward flow, upstream to downstream or inlet to outlet. If the well is back flowed prior to injection then flow is from outlet to inlet in the reverse direction and downstream to upstream! A more sensible approach is to allocate a formation and wellbore end to the plug sample and describe any flow in terms of formation to wellbore (production) or wellbore to formation (injection). This nomenclature has stood the test of time and more than 1,500 tests and avoids ambiguity in flow direction.

In-situ Permeability Measurement

It is essential that all testing can be conducted in the same apparatus. Needless offloading of plug samples and transferring to other equipment set-ups should be avoided. Permeability measurements should be made in-situ at reservoir conditions if possible. Measurements made at room conditions can be subject to artifacts and produce misleading results.

Base Permeability

Base permeability must be established in order to have a value with which to compare any after test or final permeability. The base permeability must not cause any damage in itself and so must be measured with least possible disturbance to the rock matrix. Some procedures advocate measurement of base permeability at a series of increasing rates or differential pressures across the sample. In theory, this yields a calculated permeability which is independent of the actual rate used. This is potentially damaging to the sample, as fines migration can be induced as the rate is increased. The value of all subsequent testing can be lost if damage is induced. The multiple rate or pressure measurement suggests that rates above the minimum are employed and we believe that for "return permeability" base permeability measurement this is wrong. Instead, we advocate, as outlined in SPE 38154, that for each lithology, rock type or permeability range, a base non-damaging flow rate below the critical velocity, (the flow rate which causes the onset of fines migration) for the appropriate fluid is established and permeability determined. The lowest possible rate at which meaningful data can be generated is the safest. Clearly, this rate will differ from one rock type to another. In the absence of information on critical velocity, the lowest possible rate should be used. After the simulation part of the test, return permeability is measured and provided that this measurement is made at equivalent rate or pressure to the base permeability then the data is comparable. If fines migration has occurred during drawdown or any other part of the simulation then this is a real effect and the result is valid.

Corrosion Free Hastelloy Equipment

In order to properly evaluate potential Formation Damage, it is important to incorporate all reservoirs and introduced fluids. It is essential to eliminate artifacts such as corrosion from the test as this may lead to erroneous results, conclusions and recommendations. Traditional stainless steel testing apparatus will corrode in the presence of reservoir fluids, not to mention aggressive clean up or stimulation fluids at reservoir conditions. Equipment which is contacted by fluids at reservoir conditions should be composed entirely of corrosion resistant

materials such as Hastelloy and Teflon. This eliminates any possibility of corrosion interfering with the test results.

Completion Type Planned or Options

If the completion strategy has been selected prior to the core flood tests, the design of the core flood tests must include consideration of the completion. Alternatively, core flood tests can be used to help select the optimum completion design, hardware and fluids. Normally, two sets of tests are conducted for drilling/completion operations. The first is used to screen drilling fluid options regardless of the completion fluids and hardware and the second is used to test the entire sequence from drilling through completion to production or injection.

Drilling Fluid Options

Laboratory core flood tests are often used by operating companies to help with the selection of drilling and completion fluids and hardware service providers. It is important to test any options available and to compare like with like. Fluids provided by different vendors should be designed for field use (not just laboratory test fluids) and should meet any operational requirements such as rheology, cost *etc*. Fluid properties should be fully understood in order to avoid anomalous results which can be obtained due to poor handling and preparation procedures [13].

Completion Hardware

In wells where completion hardware is deployed, this hardware must also be considered in laboratory tests. The well must be produced or injected through the composite of reservoir rock, residual mud and completion hardware in to the open well annulus. This composite must be reflected in at least some of the laboratory testing. A drilling mud may exhibit good clean-up properties when fluid alone is considered, however following gravel packing for example, the same mud or mud body may cause significant impairment and damage. The tests conducted in the laboratory must include the option to insert the completion hardware at the appropriate time in the well operations sequence.

Clean-up Options

Some tests may be conducted on the drilling fluids alone or on completion fluids alone, however, any clean-up options should be incorporated into at least some of the testing. The data presented in Table 1 is extracted from a technical paper on the Neptune development and illustrates this point clearly. Without clean-up fluids, the drilling and completion options generated significant damage. Laboratory testing showed that with appropriate clean-up fluids this damage could be significantly reduced. Test 1 shows a reduction of over 99% in permeability when no clean-up was employed. Test 2 shows a decrease of 35.6% in permeability at an equivalent point in the test when full clean-up was designed and implemented.

It is important that the clean-up fluids, and indeed any other fluid sequences, reflect real operations. Two distinct cases exist. The first is a sequence clean-up where clean-up fluids follow immediately any other introduced wellbore fluids (drilling, completion fluids). The well is then produced or injected. The second case is a remedial clean-up where the well is produced (or injected) prior to clean-up fluids application.

Although the fluids may be similar for the two different operation, the results in the field and the laboratory can be different. It is therefore essential to reflect the real operational sequence of events in the laboratory tests.

Table 1. Impact of clean-up on return permeability testing.

TEST	Fluids applied	Gravel pack1	Change in permeability after fluid application and drawdown	Change in permeability after gravel pack and mud removed	Change in permeability after spin down in ultracentrifuge
1	Base mud only	16.30	.998%	-99.3%	66.1%
2	Base Mud brine, Enzyme treatment acid treatment	16.30	356%	103%	294%

Likely Exposure Time of Formation to Any Introduced Fluids

Many field developments plans are optimized by batch drilling or batch completion of wells prior to production or injection. This process often includes long term exposure of the reservoir to introduced fluids at overbalance or balance. Introduced fluids may degrade or alter with time at reservoir conditions of temperature and pressure. Chemical or biological alteration of fluids and any changes in reservoir damage or sensitivity should be examined with long term exposure tests. Tests of increasing duration are conducted to reflect long term exposure and establish any trends in formation damage with time. Typically tests of 7, 14 and 28 days are conducted. The proposed suspension fluid or fluids should be tested.

Fluid Application

All introduced fluids such as drilling fluids and completion fluids should be applied to the wellbore face of the sample by flowing across the face at appropriate overbalance or under balance pressure and at an appropriate rate.

Drawdown

It is generally agreed that one of the key parameters in well performance and in laboratory return permeability is the progression of the well onto production (or injection). In the laboratory, two distinct methods which aim to simulate this process have been developed[5]. These are rate controlled and pressure controlled drawdown. The debate within the industry over which is the best to use will no doubt continue, we believe the answer lies in the degree to which an attempt to simulate real wellbore conditions is being made. If the testing limits its ambition to comparing the behaviour of different fluids or procedures in a laboratory test then rate controlled drawdown is acceptable. If however, we are a little bit more ambitious and are attempting to simulate real well conditions and the initial productivity or injectivity of a well, then pressure control seems to be the better method.

Rate Controlled Drawdown

After the fluid application in a coreflood test, return permeability must be measured. In order to measure a permeability comparable to the base permeability, the sample is flooded with oil, water or gas at a constant rate and pressure build-up is measured. Eventually, stable pressure is recorded, the test has reached it's end point and permeability is measured. Some authors have attributed various classifications to the pressure profiles generated and have described mud-off, lift-off and other data generated[6]. Some tests attempt to apply a rate or flux which is equivalent to real rates anticipated per unit area of wellbore. This method fails scientific scrutiny in a number of ways.

It is undeniable that a mud, mud cake or mud body which lifted or popped off the formation in large chunks would satisfy many of our well clean-up requirements. In fact, the pressure build-up and drop often described as lift-off or pop-off has many other sources including relative permeability, pump back pressure and release of filtrate. It is rare for a mud cake or mud body to lift or pop off in a laboratory test, or more importantly, in a real well.

The differential pressure profile measured across the core in flood tests by rate controlled drawdown is strongly rate dependent. A high rate will tend to produce an immediate pressure spike and then a surge as fluids break through. This process can cause rates and pressures which exceed those ever likely in the well. At a lower rate, pumped fluid will tend to percolate through the sample/mud body and without rate increase, it is unlikely that a representative saturation profile will be achieved.

When the rate is calculated for a well, it is impossible to predict the rate for each lithology. The rate will be controlled by damage which is, after all what we are trying to predict with the test!

Pressure Controlled Drawdown

In real well, the well is produced or injected by changing the well bore pressure and allowing flow to occur. This is precisely what the pressure controlled drawdown or injection test achieves. A pressure or range of pressures are selected to reflect real drawdown pressures in the well. The formation end of the sample is maintained with a large reservoir of fluid supplied at reservoir pore pressure. By dropping the pressure in the wellbore annulus of the core holder set-up, flow can be initiated through the sample if the rock and the damage allow. Normally, the rate of flow increases with time until a plateau is reached, at which point permeability to production phase can be measured. The method is much more representative of well

bore clean-up than the rate controlled method described above. It is the permeability of the rock and the extent of damage that determines flow-rate or production rate. One area of ambiguity however, is the selection of drawdown pressure or pressures. The maximum drawdown pressure once the well production will be dissipated for a great depth in to the reservoir. The length of any core plug is limited, often to about 5 cm. Once the well is flowing, only a small proportion of the drawdown pressure will be lost in the near wellbore unless there is a region of damage. At the onset of production, the majority of the pressure is likely to be taken by the very near well bore. Slowly, as the well begins to flow, the actual pressure in the near well bore area will decrease and the rate will increase. To reflect the initial period, it seems sensible to select a pressure close to the full initial drawdown to represent the pressure drop which helps to initiate flow and clean-up damage. This will give "best case" for clean-up and "worst case" for rate sensitive effects such as fines migration. Maximum drawdown pressure must never be exceeded.

INTERPRETATION

Some of the laboratory analytical procedures which can be undertaken in order to determine which mechanisms have taken place during core flood testing and their relative contribution to damage is as follows:

Pre and Post - Test Sample Evaluation

Each core plug sample at the end of the flood test is fractured lengthways into two halves, one of which is immediately cryogenically frozen under liquid nitrogen and the other half cleaned and dried by non-damaging techniques.

Untreated SEM/EDS Analysis

The trim of the core plug sample is cleaned and dried by non-damaging techniques to represent the initial state of the rock prior to the flood test, *i.e.* untreated SEM/EDS samples. This is used to determine the natural cements and clay mineralogy before analysis for comparison purposes with final dry treated samples. An example of untreated SEM analysis is presented in Figure 4.

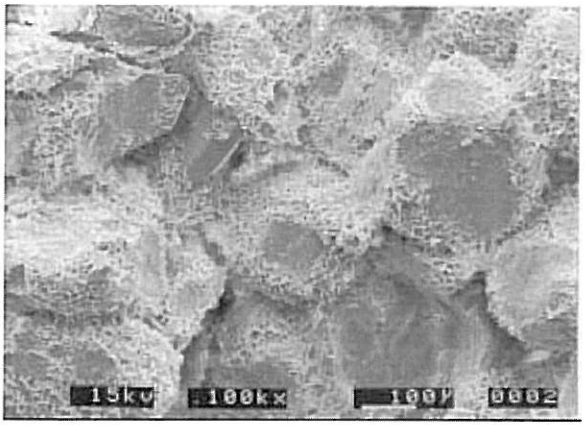


Fig. 4. Untreated SEM. The photograph shows a sample before formation damage testing. The rock grains, cements, clays and pore system can be seen and compared with the "treated' or after test samples.

Untreated Cryogenic SEM Analysis

Another off cut sample, prepared to the same initial fluid saturation profile as the respective plug, before the flood test is cryogenically frozen in liquid nitrogen and prepared and run on a cryogenic SEM. Cryogenic SEM analyses can determine the original oil/gas/formation water fluid distributions and morphologies for comparison with final treated cryogenic samples.

Untreated Thin Section Analysis

Thin section analysis of an untreated core plug trim to determine by point count analysis the mineral percentages present prior to any flood test analysis being performed.

Treated SEM Analysis

The cleaned and dried half of the core plug after the flood test is further split into wellbore and formation plug fragments. These two fragments are prepared such that the fractured surfaces are orientated perpendicular to the plug end faces. The wellbore end plug fragment can be used to check for the depth of Drilling Mud Solids invasion (see Figure 5) and together with the formation end plug fragment can be used to identify any possible fines migration and/or scale precipitates.

Treated Cryogenic SEM Analysis

The cryogenically frozen half of the core plug after the flood test is further split into wellbore and

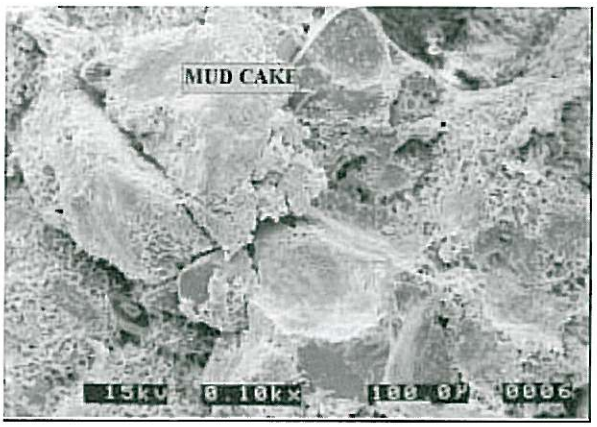


Fig. 5. Treated SEM. When comparing with the untreated sample shown in figure 4, damage mechanisms can be seen. This example shows drilling mud solids on the well bore end face towards the centre of the view.

formation plug fragments. These two fragments are prepared such that the fractured surfaces analysed are orientated perpendicular to the plug end faces. The wellbore end plug fragment can be used to check for the depth of Drilling Mud Solids/filtrate invasion and together with the formation end plug fragment is used to identify any possible soluble salt precipitation, micro-emulsion formation, fluid retention (see Figure 6) and any other immiscible fluid features.

Treated Thin Section Analysis

A longitudinal slice through the core plug sample is prepared for thin section analysis. This allows major scale precipitates, drilling mud solids invasion (see Figure 7) and fines migration to be observed. Dissolution of natural cements can also be observed.

POTENTIAL FOR USE OF LABORATORY TESTING

Most formation damage laboratory data is used for comparative purposes — Mud A versus Mud B *etc.* however, the majority of tests do attempt to reflect real well bore conditions and it should be possible to

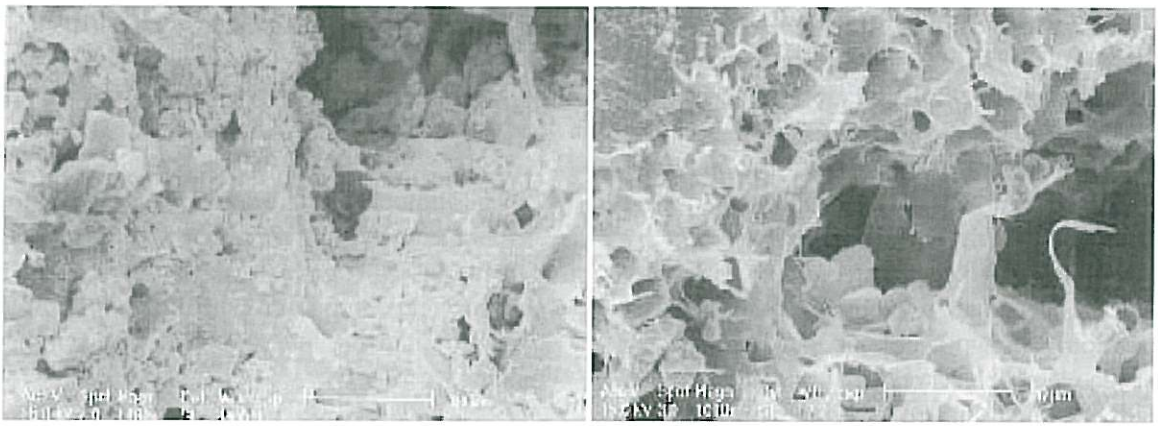


Fig. 6. Treated Cryogenic SEM. The two photographs show different levels of filtrate retention within the sample. On the left is the wellbore end / where filtrate has been retained during a core flood test, lining pores and reducing permeability. On the right the / formation end of the sample appears free of filtrate and no retention is visible.

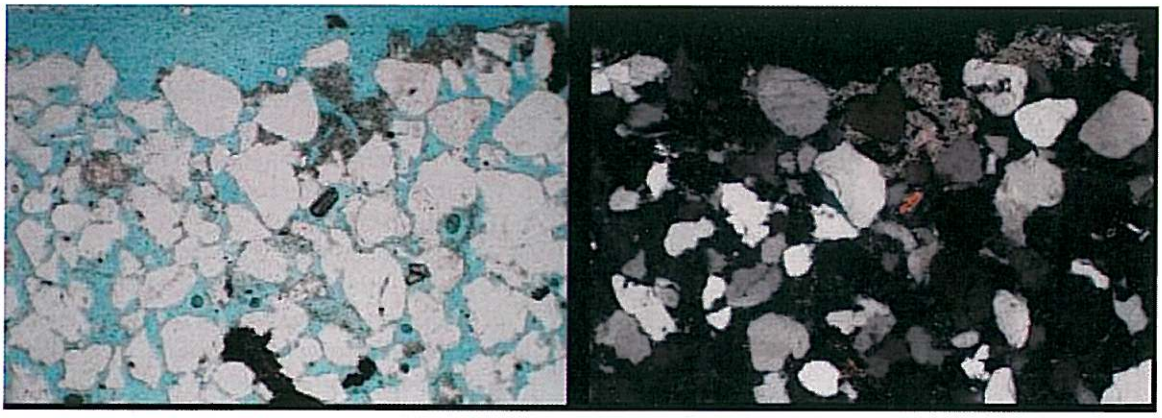


Fig. 7. Treated Thin Section. Two views of the sample sample region. The plane polarized light view on the left shows mud solids or remnant mud filter cake occluding pores at the well bore end face of the sample (towards the top right of view). A cross polarized light view on the right shows the distinctive birefringence of the calcium carbonate mud solids.

use the data to predict well performance. In theory, if all points in the well are represented and the quantity, depth and mechanisms of damage are understood, then accurate well performance prediction can be made. To achieve this objective would require analysis of test design and selection of tests to truly represent the entire wellbore. For long horizontal wells, consideration would need to be given to pressure variations along the length of the well. Overbalance will be higher and drawdown pressure higher at the heel compared to the toe. Points around the radial axis of the well should also be considered, Mud body buildup, clean-up and sand control can be different at different points in the wellbore. This variability is illustrated in Figure 8 and should be considered when laboratory tests to predict inflow performance are being designed.

Most testing is geared towards future developments of wells. Proper formation damage testing can also be used to study wells which have been drilled, completed, produced or injected. From a detailed laboratory analysis, damage mechanisms can be identified and quantified. This enables lessons to be learned and remedial treatments to be developed. In addition, old exploration well test results can be calibrated for damage based on laboratory tests and more accurate development planning can result. Many oil companies have realised that the best way to increase hydrocarbon reserves is not by exploration of new or untested acreage but by reassessment of current producing fields. Evaluation of Formation Damage problems can immediately increase recoverable reserves today and in the future, and quality testing designed to recreate the reservoir in the laboratory is a low cost solution to maximise production.

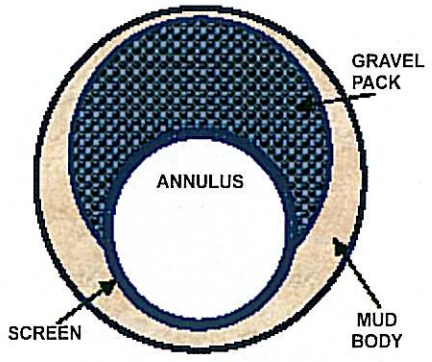


Fig. 8. Horizontal well bore schematic. Schematic diagram illustrating thicker mud body at base of horizontal. Screen sits towards the base of well and gravel fills void space. The diagram illustrates the difficulty in simulating the entire well circumference with a single linear core flood test.

CONCLUSIONS

Formation Damage laboratory tests, though simple in principle and design, are highly sensitive to the techniques and procedures employed. Careful attention to sample selection, preparation and test execution are required in order to generate data which is representative of real formation damage or stimulation mechanisms.

Through implementation of the procedures outlined in this paper, it is possible to simulate most formation damage mechanisms at reservoir conditions of temperature and pressure. Alternative procedures may be viable but those presented here give the least opportunity for anomalous results. Poor testing procedures or compromise for reasons of cost or time can lead to decisions based on incorrect results. Some of the choices and decisions made based on laboratory testing can have a significant impact on well productivity.

It is, therefore, worth the extra effort to undertake accurate tests rather than relying on tests which do not adequately simulate damage mechanisms.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the support and encouragement of Corex colleagues and management over the past fifteen years. We also thank all operating and service companies who have supported our formation damage investigations with samples and funding.

REFERENCES

[1] Marschall, D.S., Gray, R., and Byrne, M.T.,1997. Development of a recommended practice for formation damage testing. SPE European Formation Damage Conference, The Hague. *SPE* 38154 .

[2] Marschall, D.S., Gray, R., and Byrne, M.T., 1999. Permeabihty: a detailed comparative study. SPE European Formation Damage Conference, The Hague. *SPE* 54763.

[3] Byme, M, Patçy, I., Dowjis, J. and Turner J., 2002. Formate brines: a comprehensive evaluation of their formation damage control properties under realistic reservoir conditions. SPE International Symposium on Formation Damage, Lafayette. Louisiana. *SPE* 73766.

[4] Patev, I.T.M., Watson, R.B., Paveley, C. and Rushworth, P., 2001. Optimising gravel pack

performance in a high rate gas development. *SPE* 68969.

[5] Byrne, M.T., Spark, I.S.C., Patey, I.T.M. and Twynam, A.J., 2000. A laboratory drilling mud overbalance formation damage study utilising cryogenic SEM techniques. SPE International Symposium on Formation Damage, Lafayette, Louisiana, *SPE* 58738.

[6] Browne, SV., Ryan, D.F., Chambers, B.D., Gilchrist, J.M. and Bamforth, S.A., 1995. Simple approach to the cleanup of horizontal wells with prepacked screen completions. SPE European Formation Damage Conference, The Hague, May 15-16. *SPE* 30116.

Petroleum Res. J. Vol. 17 (2005); P. 25–34.

The Methodology for Selection of Corrosion Inhibitors for Oil and Gas Applications

Ian George Winning and Derek McNaughtan*

منهجية اختيار مثبط التآكل المناسب لتطبيقات النفط والغاز

ايان جورج وينج وديرك ماكنوتن

تقدم هذه الورقة مراجعة لكيفية اختيار مثبطات التآكل المستخدمة في المختبرات وحقول النفط والغاز، ولقد تم مناقشة الطرق شائعة الاستخدام في المختبرات مع التركيز بصورة خاصة على الميزات ودقة النتائج التي يتم الحصول عليها من كل طريقة. كما تم التعرض بالتفصيل إلى التطبيقات الحقلية وتقنيات المراقبة المستخدمة مع ذكر أمثلة للطرق المستخدمة حاليا وحدودها، وقورنت طريقة استخدام تقنيات الاختبار الكهروكيميائي المختلفة وكذلك العوامل الرئيسة التي يعتمد عليها في اختيار المثبط.

Abstract: *This paper reviews the laboratory and field approach in selecting corrosion inhibitors for oil and gas applications. The methods commonly employed within the laboratory environment are discussed with particular emphasis on the benefits and information each technique delivers. Field assessment and monitoring techniques are detailed with examples given on the existing methods applicability and their limitations. The electrochemical testing techniques used are compared as well as key system aspects, which influence the corrosion inhibitor selection.*

INTRODUCTION

The oil and gas industry uses corrosion inhibitors extensively for the control of corrosion to extend component lifetime as well as improving production. These products are commonly deployed in main oil export lines, subsea tiebacks and wet gas production. The treatments are usually delivered by pumping into the system continuously or as a batch treatment depending on conditions, with a typical dose rate of between 10-50 ppm based on total fluids. In the selection process, a number of test procedures must be followed before the inhibitor can be considered. This is of critical importance, as any omission or oversight in the inhibitor design can result in significant production loss from, for xample, incompatibility incompatibility of chemicals/ fluids, emulsion problems and any foaming tendency[1].

The formation and produced water generated in offshore operations can vary greatly between fields and as such has a significant effect on the corrosion rate of the pipelines. As a result, corrosion inhibitors require evaluation under conditions which simulate the field conditions as closely as possible. The water chemistry is therefore one of the first parameters to consider when selecting a suitable inhibitor. Electrochemical techniques are commonly employed for evaluating corrosion inhibitors with Linear Polarisation Resistance (LPR), the most widely used method for rapid screening[2]. Several variations exist on this method, which allows the effects of flow, temperature and pressure to be investigated. Consideration also has to be given to the persistency

* Clariant Oil Services, Scotland.

of the inhibitor. In wet gas production, the shear stresses can be relatively high creating difficulty in forming a stable film of inhibitor and accelerating its removal due to the flow regime and solids that may be in the line.

The ratio of water to crude, condensate or gas is of particular importance as this has a significant effect on whether the inhibitor recommended is water or oil soluble product and whether a continuous or batch treatment should be used[3]. The partitioning behaviour of a corrosion inhibitor between the various phases is also very important as inhibitors are normally applied on a total fluids basis and therefore need to partition into the water phase from the hydrocarbon phase to be effective. The geographical location of the production facility can play an important factor on chemical selection. Different environmental policies and restrictions can limit the options available when considering a corrosion inhibitor for deployment.

The effect corrosion inhibitors have on other production areas and chemicals in the system must also be considered. The addition of corrosion inhibitors to a hydrocarbon production system can create foaming problems particularly in turbulent conditions. In operations where low seabed temperatures are experienced, the surface-active nature of corrosion inhibitors means that they can have a negative impact on the dehydration performance of a process system, preventing chemicals added to control hydrate formation from functioning. Similarly, the stability of the inhibitor over the temperatures encountered is important as any instability could lead to precipitates and eventual blocking of the pipelines. Elastomers, used in seals, gaskets and umbilicals, can be affected by solvents causing deformation and an increase in volume or weight adversely affecting their performance.

This paper aims to identify the key inhibitor specifications and methods required to identify a corrosion inhibitor through the development of a corrosion inhibitor for a typical field application. The testing discussed in this paper details one specific application, but the methodology applied is applicable to all product development. The field monitoring options are also reviewed to identify the most suitable method for evaluating the inhibitor in the field. The main criteria for the product were as follows:

- Effective inhibition under the conditions.
- Compatibility with methanol.
- Low foaming characteristics.
- Compatibility with produced fluids.
- Compatibility with elastomers.
- High shear flow inhibition stability.

COMPATIBILITY

As part of the corrosion inhibitor design, consideration and testing is necessary for all relevant compatibility issues. These include testing for emulsion tendency, thermal stability, viscosity, foaming tendency, elastomer compatibility, compatibility of produced fluids and chemical compatibility with other production chemicals. Industry standards exist for most testing, NACE and ASTM, with operators generally setting their own protocols specific to the system in question. The methods can vary and some are more stringent than others depending on the region in question. For this application, standard test methods were employed which represented the normal practice for North Sea applications.

Water Chemistry

The brine used in this study was typical of that found in the North Sea. The composition of the brine is shown in Table 1. Sulphate and bicarbonate were replaced with NaCl to avoid any scaling interfering with corrosion measurements.

Table 1. Ionic compositions used to prepare synthetic brine.

Ion concentration	(mg/l)
Sodium	10,450
Potassium	364
Calcium	444
Magnesium	585
Barium	15
Strontium	25
Iron	12
Chloride	18,719
Sulphate	1,700
Bi-carbonate	900

Foam Tests

To evaluate the foaming tendency of the selected products, a 100 ml sample of synthetic brine was placed in a 500 ml measuring cylinder and dosed with 100 ppm inhibitor. The brine was sparged with CO_2 at a constant flow rate of 200 cm^3/min at room temperature with a sintered glass bulb used to maximise the foaming effect[4]. After 5 minutes sparging, the gas flow was stopped and the foam height and consistency observed. The time taken for the foam to collapse was then recorded.

Emulsion Tests

50 : 50 ratios of synthetic brine and standard North Sea crude were added to a graduated torpedo tube to assess the emulsion tendency with each product[5]. The inhibitors were dosed at 100 ppm under a total fluids basis and the two-phase mixture heated and held at the test temperature in a water bath for the duration of the experiments. The phases were then mixed by agitation. The colour and clarity of the interface between the hydrocarbon and brine phases were recorded at intervals of 30 seconds up to a maximum of 10 minutes.

Thermal Stability and Viscosity

A cooling bath was utilised to establish the stability of the selected products at –10°C. Each product was placed in the water bath and after 24 hours exposure removed for visual inspection. The viscosity of each product was measured at 4°C and 20°C using a Brookfield viscometer[6].

Elastomer Compatibility

Nylon 11 cylindrical coupons were immersed in each product at 115°C for a period of 21 days in accordance with ASTM D471-98 and any change in volume during that time was measured[7].

Chemical Compatibility

The compatibility of products was assessed by addition to methanol and the appearance of the solution was monitored to identify any incompatibilities. The inhibitors were dosed at rates of 0.1 %, 1%, 20 %, 50 % and 80 % on a total fluids basis.

CORROSION PERFORMANCE TESTS

Corrosion Modelling

Modelling of the field conditions was assessed before any experimental work was conducted. This was achieved by commercial software packages. This allowed the appropriate test programme to be determined by consideration of the operating minimum and maximum temperatures, partial pressure, gas ratios, water chemistry, production rates and pipe sizes to build a model of the system to be inhibited. Further information including pH, viscosity, cost and application method was then considered to assist in designing the test protocols.

Corrosion Bubble Tests

The bubble test is a CO_2 sparged beaker test used in the initial stages of an inhibitor selection programme.

The bubble test can employ a number of electrochemical techniques including Linear Polarisation Resistance (L.P.R.), Electrochemical Impedance Spectroscopy (E.I.S.) and Potentiodynamic polarization scans to assess the corrosion rate of the system. This allows rapid screening to be undertaken and identification of inhibitors that are unsuitable/incompatible with the system conditions. The effect of inhibitor concentration on performance is studied along with the time to reach maximum inhibition (adsorption kinetics) allowing the most effective candidate to be identified. Typically, bubble tests are run for 24 hours with the initial 2 hours used to establish a baseline corrosion rate for the system.

Oilfield corrosion inhibitors can take considerable time to reach maximum inhibition and an extended test period is required to determine the maximum efficiency of the inhibitor and the persistency of the film forming inhibitor. This is of particular importance in batch treatment where it may be some considerable period before the inhibitor is reapplied. The standard LPR bubble test was used to evaluate the film persistency and tenacity of the products to form an inhibiting film[8]. 1-3 hour pre-corrosion time was utilised to determine the baseline corrosion rate. The inhibitor was injected at 20 ppm and the resulting corrosion rate measured. The tests were conducted at 90°C and sparged continuously with CO_2.

Condensate from a North Sea field was also used to assess the partitioning efficiency of the inhibitor from the oil to water phase. This was conducted under differing oil to water ratios to reflect the field conditions. Other chemical additives, such as demulsifiers, scale inhibitors and hydrates, can be included to the test regime to allow assessment of their effects on the inhibitors performance. Partitioning tests were conducted at 80:20 and 20:80 brine/hydrocarbon ratios The partitioning efficiency assists in the determination of an accurate estimate of injection rate to ensure full protection in areas of water drop out or wetting. The inhibitor partitioning is based on corrosion performance rather than on an

analytical approach, although the later can also be performed. This is because the value of corrosion rate can be obtained indicating inhibitor efficiency rather than a measure of inhibitor concentration in the water which can often lead to unreliable estimates of required dosing rates.

RCE Test Method

The Rotating Cylinder Electrode test, RCE, is a standard way of performing high shear corrosion tests. For the RCE, the flow pattern changes from laminar to turbulent at high rpm speeds. The RCE enables relatively high shear stresses to be obtained in a simple cell similar to those used in bubble tests. The rotating cylinder electrode introduces turbulent flow at all but the lowest rotation speeds. With typical maximum rotation speeds of the order of 10,000 rpm, it is possible to produce shear stresses as high as 70 Pa. The RCE method is commonly employed for evaluating inhibitors in wet gas systems where high shear velocities can be expected to exist. The RCE was used to investigate the influence of flow on the inhibitors performance[9], with a rotational speed of 8000 rpm, equivalent to 52 Pa, applied. The test was sparged with CO_2 and the brine held at 80°C. 20 ppm of inhibitor was injected once a 1-2 hour pre-corrosion rate had been established.

Autoclave Test Method

For situations which demand inhibitor testing at high temperatures and pressures, greater an autoclave is used. Weight loss coupons are used to investigate general corrosion of carbon steel and stainless steel in the presence of O_2, CO_2 and H_2S. This method is also used for long term testing of the efficiency of corrosion inhibitors and allows tests at high temperature and pressure. The effects of other products, such as scale inhibitors, can be evaluated to assess change in the corrosion rate.

This apparatus allows pressures up to 200 bara and 150°C to be used in testing. Inhibitor addition can be made during a test without loss of pressure or temperature allowing a baseline corrosion rate to be established before inhibitor addition. This testing at higher pressure results in high partial pressures of carbon dioxide in solution, thus a more severe corrosion condition. A stirring facility in the autoclave enables a shear force to be applied to both weight loss coupons and electrochemical measurement electrodes. However, because of the unknown effect of the rotation of the stirring paddle on the velocity of the fluid, it is not possible to accurately quantify the wall shear stress for any given rate of stirring. This test is also able to demonstrate the ability of the inhibitor to withstand long exposure to high temperatures.

In this test the brine was pre-sparged with 100% CO_2 gas before being transferred to the autoclave and dosed with inhibitor. Coupons were cleaned with a non-abrasive cleaning liquid, rinsed with xylene and acetone, allowed to dry, weighed, and mounted on a rotating wheel inside the autoclave. At the end of the test, the coupons were removed, cleaned, weighed, and the corrosion rate calculated from the weight loss and original surface area. The testing was conducted over 48 hours at 115°C with inhibitor added at 20 and 50 ppm.

Jet Impingement

For applications where the shear stress in the system exceeds that which can be achieved by the RCE method, jet impingement testing is conducted. This method involves firing high velocity fluids through a jet to a target containing the electrodes. A series of pumps circulates the system brine through a heater which raises the brine to the field temperature before firing the brine as a fine jet onto the target. The target is fitted into a pressurised vessel which can be continuously sparged with CO_2 and/or H_2S. Inhibitors can then be assessed to determine their efficiency at extremely high shear stress. This method also allows higher temperatures and pressures to be considered when developing a corrosion inhibitor. Different electrode assemblies can be employed to establish the effects of orientation on inhibitor efficiency to simulate bends.

This technique commonly employs the LPR method for calculating corrosion and as such is not suitable in oil/brine testing. In this particular application, the shear stresses in the system were insufficient to warrant this type of testing and were therefore not conducted.

Weld Testing

Preferential weld corrosion testing can be conducted under both CO_2 and H_2S conditions. The equipment used for this testing allows the weld, heat affected zone and parent alloy to be monitored for corrosion and preferential corrosion individually. The test methods employed include LPR, galvanic current

measurements, potential measurements and EIS in low salinity brines. The evaluation of inhibitors is assessed after a pre-corrosion time varying from a few hours to several days. The test method is based on the bubble test but with far more sophisticated hardware allowing greater latitude in evaluating corrosion inhibitors. The products tested in this study were not designed for weld inhibition and therefore were not tested under this method.

RESULTS

Compatibility with Methanol

The results of compatibility tests with methanol are shown in Table 2. Products A, D, H, I J and N were found to be compatible with methanol at all levels. Products B and C were stable up to 50% with methanol but at higher concentrations clear droplets were observed to form. Product L was found to form droplets at greater concentrations than 0.1% and at higher concentrations phase separation was noted. Product M was unstable with greater than 1% corrosion inhibitor with a milky appearance observed.

Foaming Tests

The results of the foam tests are shown in Table 3. Products D, I and M were found to produce no foaming tendency. Products A, B, C, H, K, and L were found to cause an unstable flaky foam which dissipated with time, however, the height of the foam varied for each product. Product J and product N failed the test as a stable creamy foam was produced.

Table 2. Compatibility test with methanol.

Inhibitor	MeOH/CI	MeOH/CI	MeOH/CI	MeOH/CI	MeOH/CI
	99.9 : 0.1	99.1	80:20	50:50	20:80
Product A	ok	ok	ok	ok	ok
Product B	ok	ok	ok	Clear, droplets	Clear, droplets
Product C	ok	ok	ok	Clear, droplets	Clear, droplets
Product D	ok	ok	ok	ok	ok
Product E	Eliminated as inhibition was poor				
Product F	Eliminated as inhibition was poor				
Product G	Eliminated as inhibition was poor				
Product H	ok	ok	ok	ok	ok
Product I	ok	ok	ok	ok	ok
Product J	ok	ok	ok	ok	ok
Product K	Eliminated as inhibition was poor				
Product L	ok	droplets	Phase sep	milky	milky
Product M	ok	ok	milky	milky	milky
Product N	ok	ok	ok	ok	ok

Table 3. Foaming tendency.

Inhibitor	Foaming	Initial foam height	Time to collapse
Conditions: 5 min CO_2 at 200 ml/min, dose rate - 100ppm		(cm)	(min)
Product A	unstable flaky foam	5	1
Product B	unstable flaky foam	15	>10
Product C	unstable flaky foam	15	>10
Product D	Not foaming		
Product E	Previously eliminated		
Product F	Previously eliminated		
Product G	Previously eliminated		
Product H	unstable flaky foam	17	>10
Product I	Not foaming		
Product J	Stable creamy foam	4	>10
Product K	Stable creamy foam		
Product L	Stable creamy foam		
Product M	Not foaming		
Product N	Stable creamy foam	4	>10

Emulsification Testing

The crude selected for the testing was found to be strongly emulsifying and the untreated blank test required greater than 10 minutes for phase separation. The results are summarised in Table 4. Product A showed phase separation within 7 minutes. Inhibitor candidates B, C, H, J and N achieved phase separation within 4 to 5 minutes. All other products had a broad interface after 10 minutes.

Table 4. Emulsification tendency.

Inhibitor	50:50 synth. brine/ crude	water quality
25°C, 100ppm	Time to separate (min)	
blank	>10	Clear
Product A	7	Marginally worse than blk
Product B	5-4	Hazy
Product C	5-4	Hazy
Product D	>10	Yellow hazy
Product H	5	Marginally worse than blk
Product I	>10	Yellow hazy
Product J	5-4	Marginally worse than blk
Product M	>10	Yellow hazy
Product N	5-4	Marginally worse than blk

Thermal Stability and Viscosity Testing

The viscosity results are shown in Table 5. Candidates that passed the criteria were products B, C, D, H and I. Product M was found to be cloudy at –10°C and along with products A, J and N had a viscosity outside the acceptable profile.

Table 5. Low temperature stability and viscosity.

Inhibitor	Stability @ -10°C	Viscosity@ 20°C (cP)	Viscosity@ 20°C (cP)
Product A	ok	45.8	108.3
Product B	ok	63.6	67.3
Product C	ok	36.4	79.0
Product D	ok	NA	37.0
Product H	ok	35.6	80.8
Product I	ok	38.4	86.4
Product J	slightly cloudy	52.5	118.8
Product M	ok	87.0	201.0
Product N	ok	35.0	121.0

Elastomer Compatibility

The results from the elastomer compatibility are shown in Table 6. The increase in volume for Nylon 11 with inhibitors A, D, H and I were found to be between 7- 8%. A similar result was found for the weight, with an increase of between 10-14 %. The remaining products were not tested.

Table 6. Compatibility with Nylon 11.

Inhibitor	Increase in weight	Increase in volume
Conditions: 21 days, 115°C	%	%
Product A	10.90	7.07
	11.16	6.45
	11.63	6.65
Product D	13.73	7.48
	13.06	7.89
	13.86	7.89
Product H	13.08	7.68
	12.98	7.89
	13.05	7.68
Product I	11.90	6.86
	11.58	7.07
	12.03	6.65

Corrosivity Testing

All inhibitor candidates except C and L were passed on for aqueous bubble tests. The results are summarised in Table 7. The best performing inhibitors in these tests were A, B, H and M with 98 to 99% performance and good or satisfactory film persistency. D, I and J showed good corrosion inhibition but the film persistency was limited.

Partition Bubble Tests

The results of the partition bubble tests are shown in Table 8. The results demonstrate that at a water cut of 80% product A gave a corrosion rate of 7 mpy whilst product H reduced the corrosion rate to 0.9 mpy. At the lower water cut of 20%, the performance of product A had improved, reducing the corrosion rate to 0.6 mpy. Product H had a slightly poorer performance with a corrosion rate of 1.2 mpy.

RCE Testing

RCE tests were evaluated under maximum shear rate in an aqueous test at 20 ppm. Results of the

Table 7. Corrosion bubble tests.

Corrosion inhibitor	Pre-corrosion rate	Inhibited corrosion rate	Performance	Film persistency
20ppm, 90°C	(mpy)	(mpy)	%	(mpy)
Product A	205	2	99	7 stable
Product B	193	4	98	32 stable
Product C	- not tested			
Product D	175	8	95	95 raising
Product E	215	19	91	108 raising
Product F	227	77	66	201stable
Product G	216	49	77	158 stable
Product H	252	1	99	20 stable
Product I	196	3	99	85 raising
Product J	187	4	98	85 raising
Product K	217	62	71	NA
Product L	not tested			
Product M	145	2	99	14 stable
Product N	not tested			

Table 8. Partition bubble tests.

Corrosion inhibitor	Ratio brine/hydrocarbon	Pre-corrosion rate (mpy)	Inhibited corrosion rate (mpy)	% Protection
Product H	80:20	212	7	97
Product H	20:80	NA	0.6	NA
Product A	80:20	222	0.9	100
Product A	20:80	NA	1.2	NA

Table 9. RCE tests at 52Pa.

Corrosion inhibitor	Pre-corrosion rate (mpy)	Inhibited corrosion rate(mpy)	% Protection
Product A	193	7	96
Product H	204	8	96

RCE testing are shown in Table 9. Product H afforded the same level of inhibition as product A with corrosion protection of 96%.

Autoclave Testing

Table 10 shows the corrosion protection provided by product A and H in high temperature/ pressure weight loss tests. At a dose rate of 20 ppm, product H achieved around 80% corrosion protection whereas product A gave only 64% protection.

Table 10. Autoclave coupon tests.

Tests corrosion inhibitor	Pre-corrosion rate (mpy)	Inhibited corrosion rate (mpy)	% Protection
Uninhibited baseline	112.48	N/A	N/A
Product A (20 ppm)	N/A	40.72	63.80
Product H (20 ppm)	N/A	22.26	80.21
Product H (50 ppm)	N/A	22.61	79.90

SUMMARY OF RESULTS AND DISCUSSION

The pass/ fail matrix used in the Table 11 allowed rapid identification of suitable products with two strong possible candidates identified. Methanol compatibility and corrosion inhibition efficiency removed a number of potential inhibitors from the final selection process. Products E, F, G and K were found to produce insufficient inhibition while methanol incompatibility of products B, C, L and M further reduced the number. The number of possible

Table 11. Summary of the results.

Prod.	Inhibition > 90%	Persist	Methanol compatib.	Foaming	Emulsif	Thermal stability	Viscosity	Elastomer compatibility
A	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Pass
B	Pass	Pass	Fail	Pass	Pass	Pass	NA	NA
C	NA	NA	Fail	Pass	Pass	Pass	Pass	NA
D	Pass	Fail	Pass	Pass	Fail	Pass	NA	Pass
E	Pass	Fail	NA	NA	NA	NA	NA	NA
F	Fail	Fail	NA	NA	NA	NA	NA	NA
G	Fail	Fail	NA	NA	NA	NA	NA	NA
H	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
I	Pass	Fail	Pass	Pass	Fail	Pass	Pass	Pass
J	Pass	Fail	Pass	Fail	Pass	Pass	Fail	NA
K	Fail	NA	NA	NA	NA	NA	NA	NA
L	NA	NA	Fail	NA	NA	NA	NA	NA
M	Pass	Pass	Fail	Pass	Fail	Fail	Fail	NA
N	NA	NA	Pass	Fail	Pass	Pass	Fail	NA

candidates was still further reduced when film persistency, foaming tendency and elastomer compatibility were considered, discounting products D, I, J and N. This effectively left two possible candidates, products A and H. With the exception of viscosity, there was very little difference between products A and H in terms of performance. However, two further test techniques allowed a clear difference to be identified between the products. The RCE results for products A and H demonstrated that both inhibitors gave excellent inhibition at a shear stress of 52 Pa, Table 9. There was little difference between the performance, with each achieving 96 % inhibition. It was only when the autoclave results were considered that a clear difference was noted, Table 10. At the high temperature used, 115°C, product H had a superior performance. This suggests that product H would also be suitable for high temperature applications, with a dose rate of only 20 ppm affording an inhibition of 80 % in the weight loss coupons.

After careful consideration of all the key design parameters only product H fulfilled the requirements for an inhibitor for application into multiple systems. This effectively demonstrates the need for a wide ranging laboratory evaluation and the importance of non-performance testing when selecting an inhibitor for a particular system.

Field Capabilities

The assessment of a corrosion inhibitor in the field is critical to confirm the laboratory selection and performance of a corrosion inhibitor. In-situ performance in the field can be assessed by a variety of techniques. Field assessment and monitoring can be carried out by a number of methods both in-situ and back in the laboratory to allow the optimum treatment and injection rate to be established. These methods include:

- Sidestream testing
- In-line monitoring
- Electrochemical noise monitoring
- Electrical resistance based technology (ER)
- Corrosivity measurements of produced water
- Weight loss coupons
- Residual inhibitor analysis in produced water

Sidestream equipment can be used to assess the effectiveness of corrosion inhibitors in the field. The system fluids under evaluation are bypassed through the sidestream allowing varying corrosion measurement techniques to be employed including, LPR, EIS and ER probes depending on the fluids in the system. This also allows the system pressure to be monitored as well as measurement of additional relevant parameters such as temperature and concentration of dissolved oxygen in the brine. However, the flow dynamics are completely different in the sidestream as compared to the flowline or pipeline and therefore do not represent a true reflection of the system conditions.

Multiphase flow, where oil is present, limits the options for monitoring but fast response ER

technology allows multiphase systems to be evaluated in a matter of hours. This technology is routinely used to optimise inhibitor injection rates.

On line monitoring has the advantages that the actual system conditions are being assessed. However, in cases where oil is present this can often lead to fouling of electrodes making electrochemical analysis by LPR impossible. Only the longer term testing of weight loss and ER measurements are feasible in this situation. This is another application where fast response ER techniques have an advantage.

Corrosivity measurement can give good information if the rates can be measured with and without inhibitor although the system conditions of temperature and pressure are not reproduced. This method, like the analysis of residual inhibitor, is influenced by residual oil in water samples collected in the field, but can be measured quickly and easily both in the field and back in the laboratory. Samples are collected from relevant locations and then assessed in the laboratory using bubble tests. This data is compared with that originally collected during the inhibitor selection process and any anomalies noted. This test establishes that the correct dose of corrosion inhibitor is being injected into the system.

Residual corrosion inhibitor measurements are conducted in the laboratory from produced water samples from the appropriate locations. Varying analytical methods are employed to determine the concentration of corrosion inhibitor present in the produced water dependent on the type of corrosion inhibitor that has been deployed. This allows the inhibitor concentration within the water phase to be monitored and any corrective action to be taken to keep the inhibition optimised and is a secondary check on the effectiveness of the corrosion inhibitors performance.

Electrochemical noise is the natural fluctuation in potential and current occurring at an electrode interface. The processes resulting in the noise signals are related to electrode kinetics, thus for a corroding system this may be related to the corrosion rate mechanisms. Electrochemical noise is a passive monitoring technique, which means that measurements are taken from the freely corroding electrodes and do not require an externally applied signal, i.e. potential, to make the measurement. This overcomes some of the problems associated with the techniques of linear polarisation resistance and electrochemical impedance spectroscopy where the conductivity of the electrolyte, organic films, and surface scales influence the accuracy of the measurement.

Oil and water measurements are also commonly measured to determine any effect the deployed corrosion inhibitor has on the system efficiency. Any drop in hydrocyclone efficiency, due to the application of the corrosion inhibitor, could result in an increase in oil discharged overboard and violate the local environmental legislation and company policy. Compatibility of live fluids under system conditions can be also assessed in the field, allowing greater assurance of the compatibility of the corrosion inhibitor with the system.

CONCLUSIONS

- An extensive laboratory evaluation identified product H as the best performing corrosion inhibitor for the application discussed in this paper.
- The evaluation included inhibition performance testing, methanol compatibility tests, foam and emulsion tests, low temperature stability and viscosity tests.
- The importance of field data has been established in relation to optimising dose rate and ensuring the corrosion inhibitor in question is functioning as required.
- A number of field techniques have been discussed with the suitability of a particular technique identified as being dependent on the system in question.
- Of the techniques available for field assessment the most commonly employed methods are weight loss coupons, ER probes and LPR probes.

REFERENCES

[1] Poggesir, G., Hurtevent, C., 2001 (Jan.). Multifunctional chemicals for west african deep offshore fields, **SPE** 74649. SPE Oilfield Scale Symposium, Aberdeen.

[2] Papavinasam, S., Revie, R. W., Attard, M., Demoz, A., Sun, H, Donini, J. C., Michaelian,1999 (April). Inhibitor selection for internal corrosion control of pipelines: 1. Laboratory Methodologies, Corrosion NACExpo 99, 54th Annual Conference & Exposition, Texas.

[3] Swidzinski, M. Watson, J., Mackin, K., Jepson, W. P., 2003. Selection and optimization of corrosion inhibitor treatment for a new multi-phase pipeline

operating under potentially corrosive conditions, paper No. 03335, corrosion 2003, NACE international.
[4] Standard test method for foaming characteristics of lubricating oils, ASTM D892-01.
[5] Standard test method for water separability of petroleum oils and synthetic fluids. ASTM 1401-98.
[6] Standard test method for density, relative density (specific gravity), or API gravity of crude petroleum and liquid petroleum products by hydrometer method, ASTM D1298, 1998.
[7] Standard test method for rubber property-effect of liquids. ASTM D471-98, 1998.
[8] Jones, D. A., 1996. *Principles and Prevention of Corrosion*, 2nd Ed, Prentice-Hall.
[9] Webster, S., McMahon, A. J., Paisley, D. M. E., Harrop, D.,1996. *Corrosion Inhibitor Test Methods*, BP Sunbury report.
[10] Phillips, N. J., Grainger, M.,1998 (March). Development and application of kinetic hydrate inhibitors in the North Sea, **SPE** 40030. SPE Gas Technology Symposium, Canada.
[11] Jordan, M. M., Archibald. I., Donaldson, L., Stevens, K., Kemp, S.,2003 (Feb.). Deployment, monitoring and optimisation of a combined scale/corrosion inhibitor within a subsea facility in the North Sea basin. **SPE** 80214, SPE International Symposium on Oilfield Chemistry, USA.

Petroleum Res. J. Vol. 17 (2005): P. 35–42, 11 Figs.

Development of a Bullhead RPM Water Control Treatment from Laboratory to Field

Mike Singleton*, Dick Weare*, Ken Sorbie** and Robin Shields*

تطوير معالجة التحكم في المياه باستخدام محورات النفاذية النسبية من المختبر الي الحقل

مايك سنقلتون وديك وير وكين سوربي وروبن شيلدز

مع تقادم وزيادة نضج الحقول النفطية في جميع أنحاء العالم هناك تركيز متزايد على الكميات الكبيرة من المياه المصاحبة لعمليات الإنتاج وكيفية إدارتها، من الناحية الاقتصادية والبيئية. وقد تكون محورات النفاذية النسبية وسيلة بسيطة وفعالة للتحكم في إنتاج المياه دون المخاطرة بإحداث إضرار بالمنطقة المنتجة للنفط. يلقى هذا الأمر أهمية خاصة بالنسبة للآبار الهامشية حيث لا يمكن للمشغل ان يبرر إنفاق جزء مهم من الميزانية على تشخيص طبيعة المشكلة تماما وذلك بسبب أن المعالجة بالسد أو عزل المنطقة غير ممكنة في هذه الحالة.

الطبيعة الإنتقائية للمعالجة بالمحورات النفاذية النسبية تسمح بإجراء أقل تشخيص ممكن ، ولكن الدرجة التي يمكن إنقاص إنتاج المياه عندها لن تكون بذلك القدر من الأهمية كمثيلتها في المعالجة بالسد. من ناحية اخرى أثبت دراسات المحاكاة، تحت ظروف معينة ، أن تطبيق معالجات النفاذية النسبية لرأس السحب في المنطقة المنتجة (5- 10 قدم) قد تؤدي ليس فقط الى إنقاص حجم المياه المنتجة ولكن أيضا الى زيادة في إنتاج النفط.

تصف هذه الورقة مجال معالجات محورات النفاذية النسبية والمنهجية التى تتبعها شركة بيكر بترولايت في إختيار وتصميم وتقييم التطبيقات الحقلية الجوهرية ، ويتضمن هذا تقييم مختبري لتأثير المعالجة بمحورات النفاذية النسبية على قطعة نموذجية من لب الممكن وتقييم هذا الناتج المختبري علي البئر موضع البحث باستخدام نمذجة تصميمية لمعالجة قريبة من لب البئر.

من جهة أخرى نحن نرى أن تقنية المعالجة بمحورات النفاذية النسبية تمثل أحد الخيارات في مجال إدارة المياه وليست عامة التطبيق في جميع الحالات فيما يخص السيطرة على المياه.

Abstract: *With oilfields around the world becoming older and more mature, there is an increasing focus on the large quantities of water that are being produced and how these should be managed; both from an economic and environmental perspective. Relative Permeability Modifiers (RPMs) may be a simple and effective method of controlling water production without risking damage to any oil-producing zone. This is of particular interest for marginal wells where the operator cannot justify spending a significant budget allocation on fully diagnosing the nature of the problem for a blocking treatment or zonal isolation is not possible.*

The selective nature of RPM type treatments allows for a minimal amount of diagnosis to be used, however the degree to which water production is reduced will not be as significant as that for a blocking treatment. Modelling studies have shown however that, under certain circumstances, Bullhead Application of RPM Treatments in the Near Wellbore region (5-10 ft)

* Baker Petrolite, UK.
** Heriot-Watt University, UK.

can lead, not only to a reduction in the volume of water produced but also an increase in oil production.

This paper describes the area of Relative Permeability Modifier treatments and the approach that Baker Petrolite takes in the selection, design and evaluation of potential field applications. This includes the laboratory evaluation of the impact of the RPM treatment on a typical piece of reservoir core and the assessment of this laboratory response on the well in question, using a near wellbore treatment design model.

We stress, however, that we view RPM technology as simply one option in the area of water management and is not universally in all cases for water control.

INTRODUCTION

Water Management Costs and Activities

Water management is becoming an increasingly important cost issue as oilfields around the world mature and produce increasing quantities of water. Many major oil companies are now producing 50% (or greater) water in their produced fluids world-wide. The financial impact on handling such large volumes of water is extremely high, with recent estimates on the cost of handling produced water ranging from \$0.20 to \$4.00 per barrel of oil produced depending on the nature of the reservoir, the production environment etc. (Bailey[1]).

The costs discussed above account for the majority of the 'Water Management' activities listed below:

(i) The treatment and disposal of produced water.

(ii) The mitigation of the problems associated with produced water, i.e. mineral scale deposition, corrosion, demulsification, hydrates, *etc.*

(iii) The reduction in water production through the application of chemical or mechanical water shut-off techniques, including downhole separation.

(iv) The prediction of oil and water displacement and production, through simulation and modelling.

(v) The handling and treating of produced water specifically for re-injection (PWRI = Produced Water Re-Injection).

(vi) Intervention to reduce produced water by global field changes to well injection/production strategies. This is more of a reservoir management approach.

(vii) Installation of "intelligent" wells, which will respond to their environment using various sensors and will adapt by shutting off water-producing completions. These systems are likely to be introduced some time in the future.

(viii) The treatment of water for secondary recovery (water flooding). Though not strictly a produced water handling cost, it is still a Water Management activity that requires resources.

Baker Petrolite is particularly active in mitigating the problems associated with produced water (scale, corrosion, demulsification, *etc.*) and has interests in treatment of water for injection during secondary recovery (including Produced Water Re-Injection) and disposal (items i – iii and vi). There are, however, areas where the industry perceives that improvements in current technology are required and one of these is Chemical Water Control, in particular the application of Relative Permeability Modifiers.

Chemical Water Control Treatments

The origins of water production problems in reservoirs may be generally classified as due to matrix production (arising from the heterogeneity of the formation) or due to fractures (this can include cracks in production casing or the failed cement jobs) (Elphick[2]). The water source may be injected or may be due to an active aquifer. For the purpose of this paper only water production from matrix systems will be discussed.

The problem of a single reservoir zone producing 100% water with all other, non-communicating zones producing oil, has been identified by a number of engineers in the industry as being essentially solved (~80% success rate). The water producing zone can be mechanically isolated and the relevant gel treatment injected to completely block off the zone (Sydansk[3] and Seright[4]). Although this is a relatively simple case, it still requires extremely good diagnosis of the position of the water zone and a considerable amount of mechanical intervention to isolate it. Failure to achieve either of these design tasks can lead to gel misplacement and damage to the surrounding oil producing zones.

Although the problem and treatment described above is relatively simple, the application of such technology can be cost-prohibitive. The large amount of diagnosis required in identifying the water producing zone (production logging tools *etc.*) and the engineering needed to isolate it (packers/coiled tubing *etc*), which greatly increase the chances of

success, can be expensive. Since most wells that require such a treatment are in their later life, the budget allocation that they have for remedial treatments may not be sufficient to cover these costs. In addition to the cost implications there are also well configurations where complete isolation of the water production zone is not possible (*e.g.* where gravel packs or sand screens have been used to minimise sand production).

A preferable option to minimise these complications, is to use a chemical treatment, known as a Relative Permeability Modifier (RPM) that can be bullheaded into the near well formation (Nieves[5], Faber[6], Zaitoun[7] and Zaitoun [8]). These chemical treatments are currently available and are known to restrict the flow of water more significantly than oil. However, they have also been found to have had sporadic success when applied in the field (approximately 40 - 50% success rate for the simple case discussed above). It is generally acknowledged that most matrix water production problems are more complicated than that discussed above and can contain simultaneously, 100% oil producing zones, two-phase (oil/water) production zones, layers of 100% water production, cross flow between different geological strata and possibly production of bottom water (aquifer).

Several studies have been performed to try and understand the mechanisms by which these materials work (Liang[9] [10], Mennella [11] and Singleton[12]. Improving the probability of success of these RPM treatments is one of the major challenges of chemical water control. The objective of this paper is to discuss the strategy that has been developed by Baker Petrolite in the evaluation and design of such RPM treatments for field application.

WATER CONTROL TREATMENT DESIGN STRATEGY

In order to correctly design and apply a successful Water Control Treatment several areas have to be addressed. These include defining the treatment philosophy and criteria for success, having a full understanding of how the chemical treatment interacts with the reservoir core and fluids (including permeability reductions to oil and water) and how these permeability reductions influence oil and water flows in a field production environment. This latter aspect is addressed by the use of a near wellbore treatment design model, where in addition to evaluating the impact of the permeability reductions, the treatment volumes and placement parameters can be optimised. These steps are now discussed in turn with a field example to illustrate the process.

Treatment Philosophy

From the previous discussion, comparing blocking treatments with those using Relative Permeability Modifiers, it is apparent that complete shut-off of the water production is an extremely difficult and risky task in terms of the potential loss of oil production. The treatment design philosophy that has been developed is to consider RPM/Water Control Treatments in a similar manner to Scale Inhibitor Squeeze treatments that are routinely performed in the field. Instead of aiming to completely shut-off water production, the RPM treatment is designed to a lower risk option that will yield "modest" reductions in water production with a subsequent increase in daily oil production over a period of ~200 days (around 6 months). Simulation studies have indicated that, under certain circumstances a reduction in the volume of water produced from the well will automatically yield an increase in oil production by advancing already available oil and adding incremental oil through improved sweep efficiency. An example of the predicted response of a production well to a Water Control Treatment is shown in the plot below (Fig. 1).

RPM CHEMISTRY

The Relative Permeability Modifier chemistry is a two-component system, which will enter the near wellbore formation in its un-reacted liquid state. Over the shut-in period (nominally 16hrs), this gelant solution is converted into a weak gel, which will "lip" out of the bottle holding it. This is in contrast with

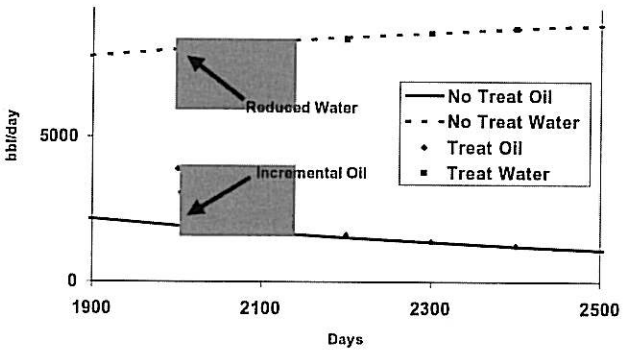


Fig. 1. Predicted treatment response for a production well.

the physical state of a blocking gel, which once gelled, will not flow from the bottle containing it. Examples of these two contrasting gel states are provided in the photographs below (Fig. 2).

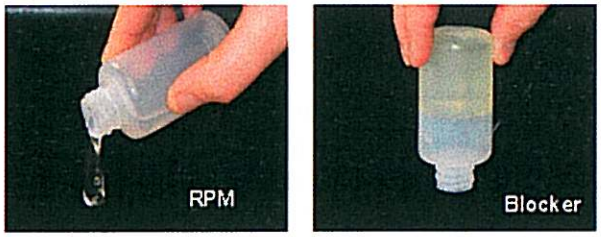


Fig. 2. Physical comparison of RPM Gel vs. a blocking gel.

Laboratory Evaluation

The main method of evaluating the impact of a Water Control Treatment in the laboratory is the use of coreflood experiments using oven housed coreflood rigs, shown schematically in Figure 3.

The experiments are performed under reservoir conditions, ideally using reservoir core and fluids, however when these are not available Clashach sandstone, iso-alkane oil and synthetic brines are used. The differential pressure across the core is recorded on the computer via the differential pressure transducer as Oil, Water and Treatment are pumped through it core during the various stages of the experiment:

(i) Water flow at 100% Water Saturation.
(ii) Pre-Treatment Oil Flow at Residual Water Saturation (S_{wi}).
(iii) Pre-Treatment Water Flow at Residual Oil Saturation (S_{or}).
(iv) Treatment Injection.
(v) Post Treatment Water Flow at Residual Oil Saturation (S_{or}).
(vi) Post Treatment Oil Flow at Residual Water Saturation (S_{wi}).

Measurement of the differential pressure across the core during steady state oil and water flow allows the permeabilities of both oil and water to be calculated for the various stages of the experiment, using Darcy's Law. The effectiveness of the treatment on modifying the relative permeabilities to oil and water are then quantified in terms of a Resistance Factor to oil or water flow (RF_w and RF_o respectively). These are defined as the ratio of the water (oil) permeabilities, k_w (k_o), before the polymer treatment to that following it.

i.e.

$$RF_w = \frac{k_w(at\ S_{or};\ pre-treatment)}{k_w(at\ S_{or};\ post-treatment)} \quad (1)$$

and

$$RF_o = \frac{k_o(at\ S_{wi};\ pre-treatment)}{k_o(at\ S_{wi};\ post-treatment)} \quad (2)$$

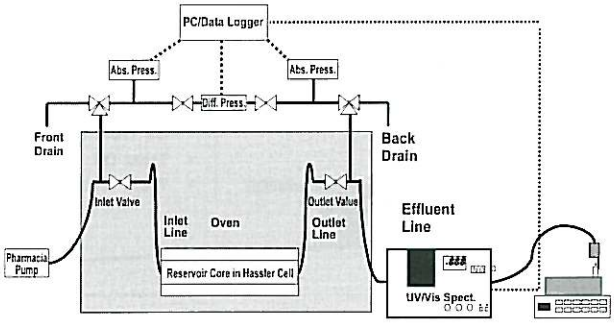


Fig. 3. Schematic of coreflood apparatus used to evaluate treatment performance.

RPM Treatment Performance

During the development of the RPM treatment a series of coreflood experiments were performed to assess the effectiveness of the treatment in terms of Resistance Factors to Water and Oil on Clashach sandstone of various permeabilities. The Resistance Factors that were recorded for this series of experiments are summarised in the plots below (Figs. 4 and 5).

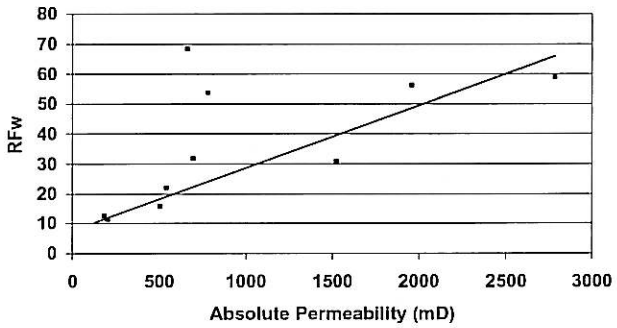


Fig. 4. Relationship between resistance factor to water and core absolute permeability.

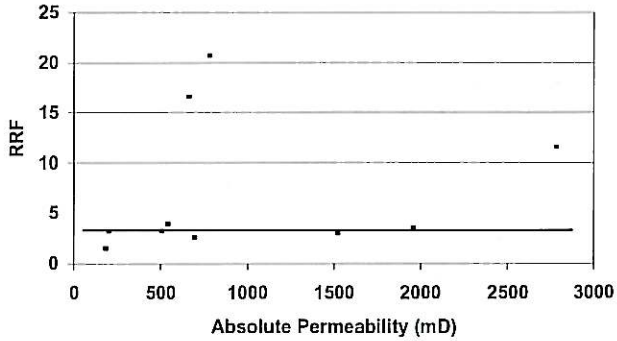


Fig. 5. Relationship between relative resistance factor and absolute permeability.

The Resistance Factor to water was found to increase as the absolute permeability of the core increased (Fig. 4). This was a surprising result and was in contrast to the results/trend that are quoted for a polymer only treatment. For polymer treatments, where a polymer layer thickness restricts water flow, its impact is diminished as the pore size (and permeability) increases. For gel treatments, a similar post treatment permeability was achieved for all cases and as a result the resistance factor that was achieved was greater for the cores with a larger initial permeability than those for a lower permeability.

Figure 5 summarises the impact of the treatment on oil permeability relative to the absolute permeability of the core. This is achieved by plotting the Relative Resistance Factor - RRF (defined as the ratio of RF_w/ RF_o) against Absolute Permeability. The general trend that was observed from these results was that the oil permeability reduction achieved was a factor of three lower than that achieved for water. There were a few outliers to this trend, however these were loaded in favour of RF_w.

Laboratory Evaluation of a Field Case

In order to design a field application of the RPM treatment it is necessary to assess the impact of the treatment under field conditions (Temperature, Permeability, Fluids *etc.*). For the field case that is to be discussed in this paper, no reservoir core or oil was available to perform the experiment. It was therefore necessary to use Clashach sandstone core (150mD) and synthetic oil (0.8cP) that matched that present in the field. The experimental method and apparatus used was that discussed above.

The resistance factors that were achieved for this application were found to be 13 for water (RF_w = 13) and 3 for oil (RF_o = 3). These reductions were then mathematically applied to the relative permeability curves that were supplied by the operator. The pre and post treatment permeability curves are plotted in Figure 6.

TREATMENT DESIGN – NEAR WELBORE MODELLING

Candidate well selection is a critical part of the Water Control Treatment process. Failure to identify the correct candidate well can lead to treatment failure and in certain circumstances a substantial loss of oil

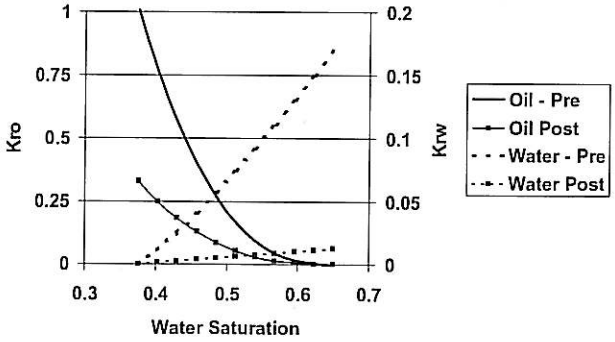


Fig. 6. Field case relative permeabilities: pre and post treatment (RF_w = 13 and RF_o = 3).

production. As a result of this, each potential treatment is evaluated prior to application.

This evaluation and the optimization of the treatment to be applied, is performed by a PC based Near Wellbore Model, similar to the SQUEEZE V design model that was developed by Heriot-Watt University for scale inhibitor squeeze treatments. The model has the ability to simulate the following phenomena:

(i) Oil and Water flow through the near wellbore formation.
(ii) Chemical injection and placement. Both of these are dependent on the properties of the chemical package and the formation rock, and also the treatment design (i.e. pre and post-flush size, pump rate etc).
(iii) The mechanisms by which the chemical is retained and how the chemical returns (adsorption/retention).
(iv) The effect of the retained chemical on the permeability of the formation rock to oil and water and how these changes affect the overall production rate.

This process enables the well technologist or production chemist to maximise the treatment's potential for success and establish its economic viability over a lifetime of 6 months.

Methodology

The methodology by which the evaluation and optimization takes place is as follows: The well details, including completion details, production rates, fluid properties, layer permeabilities and water saturation profile in the near wellbore region (estimated or from a reservoir model) are input into the data set. The producing well is then put onto production at the current production rate until the pre-treatment water cut has been established. At this point the treatment is injected into the near wellbore

formation, where it penetrates the various producing layers based upon their permeabilities. In general, the treatment volume that is injected has been designed to ensure that the first five feet of the near well formation are penetrated, however this can be reduced depending on the response of the well. The oil and water relative permeability curves are then reduced by the pre-defined Resistance Factor (RF_o and RF_w respectively) based upon where the treatment has invaded the formation. The well is then returned to production and the resulting production profile is compared to what would have taken place if no action (treatment) had been taken.

The effectiveness of each well treatment is assessed by comparing oil and water production, over a period of 200 days following the treatment, to what would be achieved if no treatment were applied. The economic value of the treatment in terms of increased oil and reduced water production is then calculated based on the assumptions of the value of a barrel of oil ($20 per barrel) and the cost of handling a barrel of water ($0.25 per barrel). These values may vary depending on the current financial and operating conditions, however it is felt that the above values are suitable assumptions for this purpose.

N.B. It must be noted that no costing assumptions have been made in this assessment.

For example, if a well has an increased oil production of 1000 bbls, with water production reducing by the same amount the value of the well will be increased as below.

1000 barrels additional oil		
@ $20 per bbl	=	$20000
1000 barrels less water		
@ $0.25 per bbl	=	$2500
Well Value added over 200 days	=	$22500

Field Case Evaluation – Well "A"

The well to be discussed below is a candidate well, which is to be treated with the RPM treatment. It has three producing intervals with layer heights and permeabilities of 3ft, 14ft, 37ft and 20mD, 40mD and 80mD respectively. It has a daily production rate of 142bbl/day at a water cut of 84%. Figure 7 summarises its layer geometry.

A 60 bbl treatment volume is injected into the near wellbore region. This volume was initially calculated to achieve a uniform penetration of 5ft into all three layers. As can be seen in the Resistance Factor distribution plot below (Fig. 8), the heterogeneity of

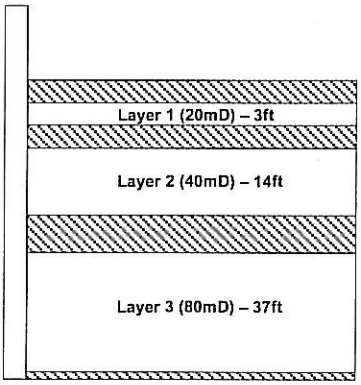


Fig. 7. Layer geometry of field case well "A".

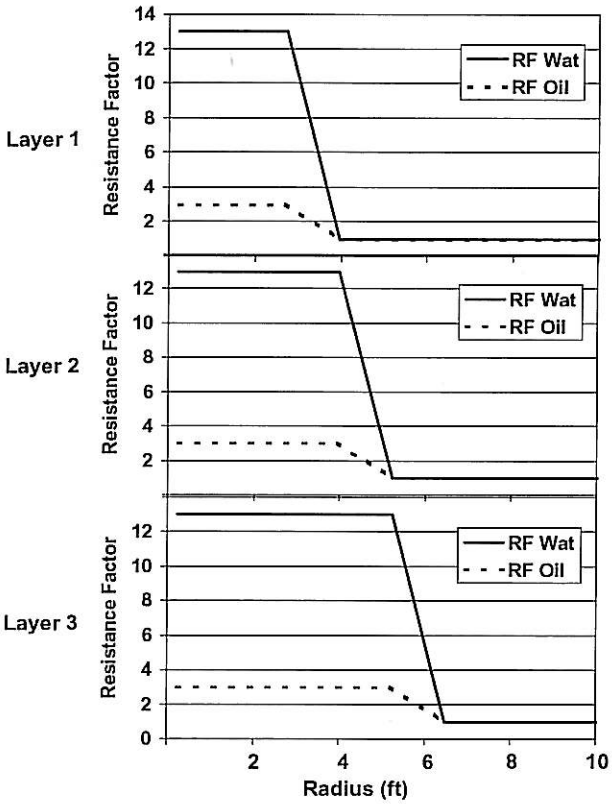


Fig. 8. Distribution of resistance factors from near wellbore model.

the near wellbore formation causes a variation of the treatment penetration based upon their respective permeabilities and layer heights (3ft, 4ft and 5.5ft respectively). From the laboratory evaluation discussed previously resistance factors of 13 and 3 for oil and water respectively are applied to the formation, which has been exposed to the treatment based upon the treatment penetration discussed below. In addition to the distribution of resistance factors, the model is capable of monitoring the distribution of water saturations, chemicals (scale inhibitors or tracers) and treatment in the near wellbore, however due to limited space it has not been possible to present these here.

The evaluation of the well's response to this treatment is plotted in Figure 9 below. By comparing the treated and non-treated production volumes for oil and water, water production is seen to be reduced by ~900bbl with a corresponding increase in oil production of ~900bbl, over the 200 day lifetime of the treatment. This predicted outcome would yield a value of ~$20,000 based upon the assumptions made upon the value of oil and the cost of handling the produced water. This predicted outcome is only possible if the pre-treatment production rate is maintained following the treatment. Application of a Water Control Treatment by definition will restrict the ability of fluid to flow from the formation. In order to maintain the pre-treatment production rate it is therefore necessary to increase the differential pressure across the formation – i.e. increase the well's drawdown. In the case of Well "A" this equates to an increase of ~1000psi (69 bar).

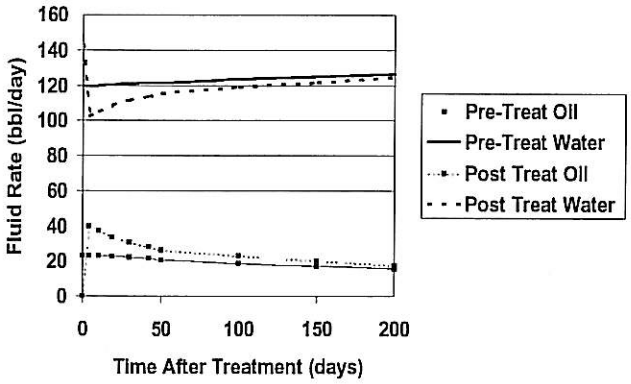


Fig. 9. Post treatment production response for well "A".

Field Case Evaluation – Well "B"

Well "B" is an illustration of the response of a poor candidate well. This well is a duplicate of that discussed above (Well "A"), however the heterogeneity observed there is not seen in this case with all three layers possessing the same permeability of 60mD.

The response of Well "B" is plotted in Figure 10. In contrast to the heterogeneous formation, Well "B" responds poorly. The treatment does reduce water production by ~110bbl however, to achieve this oil production also reduced by 163bbl. This is due to the inability of the well to maintain its pre-treatment production rate. The maximum draw down is applied to the well, however this is still not sufficient to maintain production.

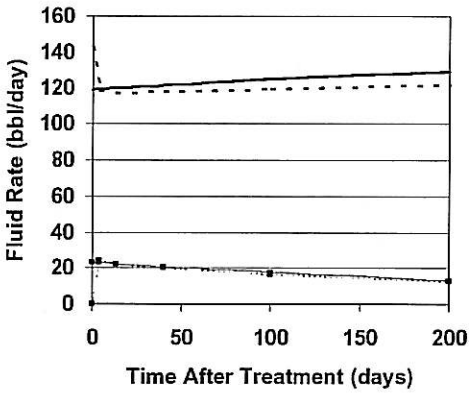


Fig. 10. Post treatment production response for well "B".

Theoretical High Volume Production Case Evaluation – Well "C"

This case was evaluated to illustrate the potential of applying RPM treatments to high volume production wells. The formation in question is a 3-layer system with each layer being 50ft deep. The top and bottom layers have a permeability of 200mD with the middle layer possessing a permeability of 1000mD. The production rate of the well is 10,000bbl of fluid per day with a water cut of 80%.

The same treatment as that discussed above was applied to this well to achieve a penetration depth of 5ft (500bbl). The resistance factors that were set up on gelation were also the same as those used for Wells "A" and "B" – RF_w = 13 and RF_o = 3. By maintaining the production rate at 10,000bbl of fluid per day the treatment is predicted to result in 58,000bbl less water and an additional 58,000bbl of oil, which corresponds to $1.2 million of added value to the well. The response is summarised in Figure 11.

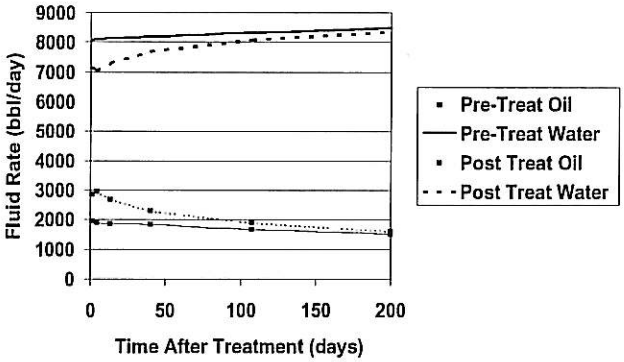


Fig. 11. Post treatment production response for well "C".

SUMMARY

Baker Petrolite, working closely with Heriot-Watt

University, has developed an approach for the design and evaluation of a RPM treatment package that is a combination of experimental core flooding tests, near well modelling and chemistry. The combined understanding of how reservoir and chemical properties influence the success or failure of a treatment and the ability to model several treatment scenarios provides a novel approach which will help to improve the success rate of RPM treatments and provide significant value to the customer.

This approach is currently in the field validation phase and Baker Petrolite are currently pursuing several field trial opportunities which will be reported on in due course.

REFERENCES

[1] Bailey, B. *et al.*, 2000. "Water Control" Oilfield Review- Spring, p. 30-51.

[2] Elphick, J. and Seright, R.S., 1997 (August). A classification of water problem types. Paper 1 presented at the 1997 PNC 3rd International Conference on Reservoir Conformance, Profile Control, Water and Gas Shut Off.

[3] Sydansk, R.D. and South well, G.P., 1998. SPE 49315: more than 12 years of experience with a successful conformance-control polymer gel technology. SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana.

[4] Seright, R.S. and Liang, J., 1998. SPE 26991: a survey of field applications of gel treatments in water shut-off: 3rd Latin American/Caribbean Petroleum Engineering Conference, Buenos Aires, Argentina.

[5] Nieves, G. *et al.*, 2002 (April). SPE 75123: Field application of Relative Permeability Modifier in Venezuela", presented at the SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma. 13-17.

[6] Faber, M.J., *et al.*, 1998. SPE 39633: water shut-off field experience with a relative permeability modification system in the Marmot Field (Oman), SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma.

[7] Zaitoun, A., Rebar, R., and Kohler, N., 1991. SPE 22785: thin polyacrylamide gels for water control in high permeability production wells. 66th Annual Technical Conference and Exhibition of the SPE, Dallas, Texas.

[8] Zaitoun, A. *et al.*, 1999 (Oct.). SPE 56740: water shut-off by relative permeability modifiers: lessons from several field applications: SPE Annual Technical Conference and Exhibition, Houston, Texas.

[9] Liang, J., H. Sun, and Seright R.S., 1995. (Nov.). Why do gels reduce water permeability more than oil permeability. *SPE Reservoir Engineering*, 282-286.

[10] Liang, J. and Seright R.S., 1997. SPE 37249: further investigations of why gels reduce K_w more than K_o: SPE International Symposium on Oilfield Chemistry. Houston, Texas.

[11] Menella, A., *et al.*, 1998. SPE 39634: pore-scale mechanism for selective permeability reduction by polymer injection. SPE/DOE Improved Oil Recovery Symposium. Tulsa, Oklahoma.

[12] Singleton, M.A., Sorbie, K.S. and Shields, R.,2002. Further development of the pore scale mechanism of the relative permeability modification by partially hydrolysed polyacrylamide: SPE/DOE 13th Symposium on Improved Oil Recovery. Tulsa, Oklahoma.

Petroleum Res. J. Vol. 17 (2005); P. 43–46, 8 Figs.

Role of Steel Surface Finish on the Performance of Sodium Nitrite Inhibitor

Tala Abohalguma, F. El shawesh, Naiema Elahresh and W .BinZiglam*

دور نعومة عينات من الفولاذ عن أداء المثبط نيترات الصوديوم

تالة أبوحلقومة وفوزي الشاوش ونعيمة الأحرش ووليد بن زقلام

لقد تم دراسة دور نعومة أسطح عيّنات من الفولاذ تعرضت لدرجات مختلفة من النعومة في أداء تراكيز مختلفة (100,400 and 800 ppm) لمثبط التآكل نيترايت الصوديوم عند درجتي الحرارة 2±70 °م، 2±22 وذلك باستخدام طرق كهروكيميائية (طريقة مقاومة الاستقطاب الخطي).

بيّنت النتائج المعملية أن العيّنات الفولاذية ذات السطح الخشن (100grit) لها مقاومة استقطاب (Rp) منخفضة أي معدل تآكل عالي ويزداد هذا المعدل بانخفاض تركيز المثبط . أما بالنسبة لعينات الفولاذ ذات الأسطح الملساء (100grit) فان النتائج أظهرت معدلات تآكل منخفضة (مقاومة استقطاب مرتفعة) حتى عند استخدام التركيز المنخفض 100grit من المثبط . كما لوحظ بوجه عام انخفاض مقاومة الاستقطاب أي ارتفاع معدلات التآكل لجميع العينات المدروسة عند درجة الحرارة المرتفعة (2± 70°).

ABSTRACT : *The role of surface finish of carbon steel samples subjected to different degrees of surface finish (as received, ground and ground and corroded), on the performance of sodium nitrite inhibitor (100, 400 and 800 ppm), at temperatures (22± 2° C) and (70 ± 2° C) was assessed using different electrochemical test techniques.*

Rough ground samples (100 grit paper), showed pronounced corrosion attack (low Rp). The severity of corrosion attack was more pronounced when tests were conducted in aqueous solution containing low concentration of inhibitor (100 ppm). In contrast, low to/or no corrosion attack (high Rp/ inhibitor efficiency) was observed when carbon steel samples were subjected to soft grinding using 1000 grit paper. This was observed even when tests were conducted at inhibitor concentrations as low as (100 ppm).

Marked decrease in the inhibitor efficiency was recorded for ground and corroded carbon steel samples even when samples were ground at 1000 grit paper.

Generally, tests at high temperature of (70 ± 2° C) observed to reduce the inhibitor efficiency.

INTRODUTION

Many types of aqueous corrosion inhibitors are being used to combat the corrosion of steel in water and oil mediums such as cooling water system and oil / gas production facilities respectively.

The interaction of corrosion inhibitor with clean steel surface seems to be well known. However, it is difficult to get a clean surface of steel in cooling water system which is in contact with neutral aqueous solution. There are many types of corrosion attack encountered in the cooling system. One type of corrosion attack is known as under deposit corrosion attack.[1-3] This was historically the source of many equipment failures as a result of pitting corrosion that

* Petroleum Research Centre, P.O. Box 6431, Tripoli, Libya.

can lead to perforation thus requiring a premature replacement of the failed equipment.[4] Smooth surface finish samples require low inhibitor concentration and the build-up of a passive film is expected to be adherent, coherent and homogenous.[5,6] In addition to that the presence of oxide film mix of hydrated FeO and Fe_2O_3 is expected to reduce the rate of nitrite adsorption on the sample surface and the formation of continuous, adherent and regular passive film.[6,7] Iron has a tendency to precipitate with an ions within the environment on the metal surface. The impact of iron oxide deposits on the over all corrosion control process is two fold. First the deposit of iron oxide creates a self-perpetuating corrosion reaction, where by a differential result in under the deposit corrosion. Localized corrosion attack (pitting) which in turn reduces the effectiveness of corrosion inhibitors by preventing them from reaching the metal surface. The second possibility is the incorporation of non protective iron oxides into the corrosion inhibitor film.

At high temperature a reduction in physicochemical properties of the inhibitor as well as the diffusion of oxygen to the metal surface are expected to be markedly affected. The oxygen carried molecules of sodium nitrite is expected to vanish with the increase of temperature and less quantity of inhibitor is expected to adsorb at metal surface.[8]

The objective of this paper is to assess the role of metal surface finish on the efficiency and/or performance of sodium nitrite as a passive film corrosion inhibitor at room temperature (22± 2° C) and (70 ±2° C) using electrochemical technique.

EXPERIMENTAL METHOD

The effect of surface finish on the performance of sodium nitrite inhibitor ($NaNO_2$) was assessed using electrochemical technique. Linear polarization resistance (LPR) was measured at each test condition and from that a corrosion rate was calculated. Mild steel samples having a chemical composition as shown in Table 1 were subjected to the following surface treatment:

1-Samples ground on two grades of emery papers (100 and 1000 grit paper).

Table 1 . Chemical composition of used mild steel samples (wt. %).

UNC	AISI	C	Mn	Pmax	S_{max}
G10180	1018	0.14 -0.20	0.60 - 0.90	0.040	0.050

2-Samples ground at 100 and 1000 grit paper and afterward corroded by inserting them in tap water for 72 hours. The corroded samples were then removed and dried before being tested.

All corrosion tests were conducted using distilled water with various concentrations of sodium nitrite inhibitor (blank, 100, 400, and 800 ppm) and temperatures of (22±2° C & 70 ±2° C) using potentio-dynamic test technique.

RESULTS AND DISCUSSION

The test results of the effect of surface finish on the performance of sodium nitrite inhibitor at 22±2° C and 70 ±2° C are shown in Figures 1-8. Figures 1 and 2, exhibit the effect of grinding of test samples, at different paper grades (100 and 1000 grit paper), on the performance of sodium nitrite inhibitor at room temperature. When tests were carried out, at highest concentrations of corrosion inhibitor, it was observed that samples with very smooth surface finish (1000 grit paper) showed a very high polarization resistance (Rp) value ($\approx$ 550,000 ohm.cm^2) compared with (Rp $\approx$ 70,000 ohm.cm^2) for sample ground at (100 grit paper). In addition to that samples with smooth surface finish showed higher values of Rp (120,000 ohm.cm^2) at low inhibitor concentration of 100ppm compared with (42,000 ohm.cm^2) obtained for samples ground at (100 grit paper). This can be contributed to the fact that smooth surface finish samples require low inhibitor concentration as well as the built-up passive film is expected to be adherent, coherent and homogenous.[5,6] In contrast, the surface finish for samples ground at 100 grit paper is expected to be rough and irregular as result of confined plastic deformation. Therefore, high inhibitor concentration is required to cover the non uniform steel surface. [5,6]

Marked reduction of Rp was reported when samples were ground (100 and 1000 grit papers) and corroded then tested in the same above condition, as shown in Figures 3 and 4. This was pronounced for grind (1000 grit) and corroded samples, where ten fold reduction in Rp was reported at corrosion inhibitors concentration of 800 ppm , as shown in Figure 4. This can be attributed to the presence of corroded sites over the test samples, where high quantity of inhibitor is required. In addition to that the presence of oxide film mix of hydrated FeO and Fe_2O_3 is expected to reduce the rate of nitrite adsorption on the sample surface and formation of continuous, adherent and regular passive film.[6,7]

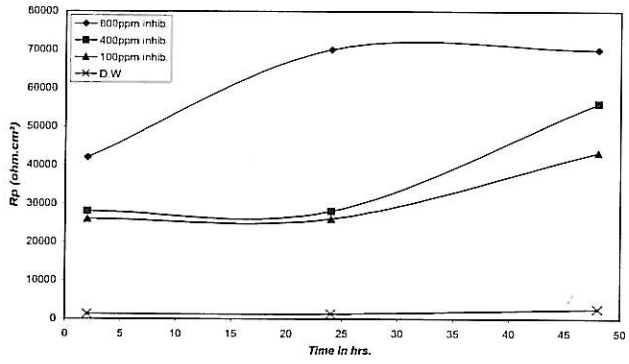


Fig. 1. Relationship between Rpxs values and duration time for samples ground (100 grit paper) and tested at room temperature (22±2° C) over various inhibitor concentrations.

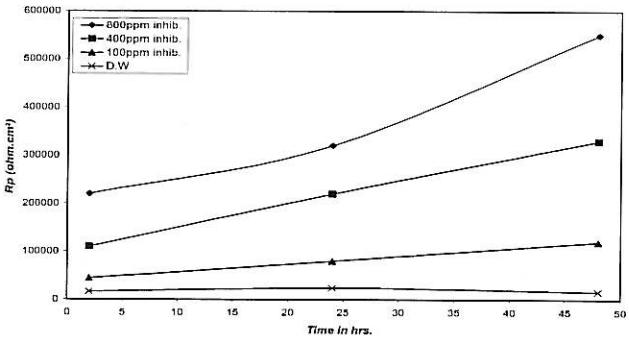


Fig. 2. Relationship between Rpxs values and duration time for samples ground (1000 grit paper) and tested at room temperature over various inhibitor concentrations.

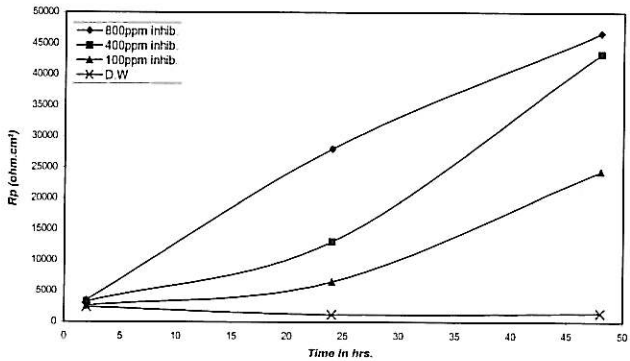


Fig. 3. Relationship between Rpxs values and duration time for samples ground (100 grit paper) and rusted then tested at room temperature over various inhibitor concentrations.

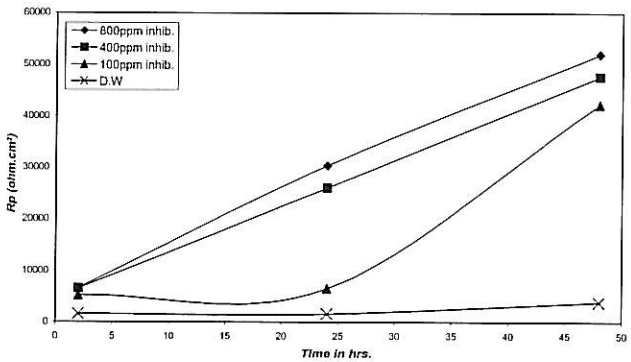


Fig. 4. Relationship between Rpxs values and duration time for samples ground (1000 grit paper) and rusted then tested at room temperature over various inhibitor concentrations.

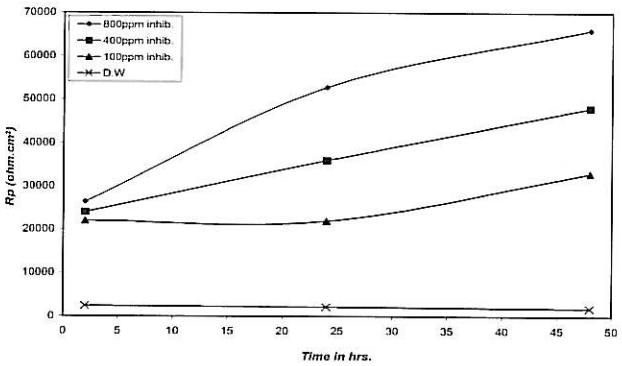


Fig. 5. Relationship between Rpxs values and duration time for samples ground (100 grit paper) and tested at (70± 2° C) over various inhibitor concentrations.

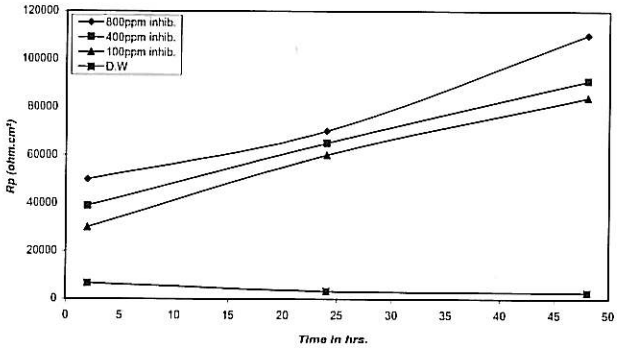


Fig. 6. Relationship between Rpxs values and duration time for samples ground (1000 grit paper) and tested at (70 ±2° C) over various inhibitor concentrations.

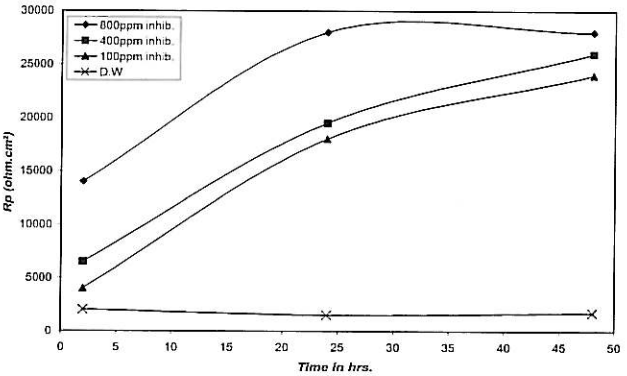


Fig. 7. Relationship between Rpxs values and duration time for samples ground (100 grit paper) and rusted then tested at (70 ±2° C) over various inhibitor concentrations.

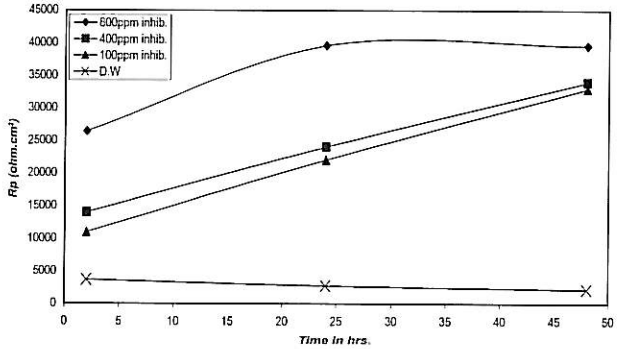


Fig. 8. Relationship between Rpxs values and duration time for samples ground (1000 grit paper) and rusted then tested at (70 ±2° C) over various inhibitor concentrations.

In contrast less marked reduction of Rp was reported for ground (100 g) and corroded samples, where two fold reduction of Rp was reported at 800 ppm inhibitor concentration (Fig. 3) compared with ground samples only, (Fig. 1). This can be attributed to the low Rp values for samples ground at 100 grit paper.

Tests at high temperature of (70 ± 2° C) caused marked reduction of Rp or inhibitor efficiency as shown in Figures 5 to 8.Tests at this temperature with an inhibitor concentration of 800ppm result in low Rp value (110,000 ohm.cm^2) for samples ground at 1000 emery paper compare with tests conducted at 22±2° C where high Rp value (550,000 ohm.cm^2) was observed. In contrast, ground and corroded samples (100 and 1000 grit papers) showed much less Rp values (low inhibitor performance) when tested at various inhibitor concentration, as shown in Figures 7, 8. This can be attributed to the fact that the tests at high temperature caused a reduction in physicochemical properties of the inhibitor as well as the diffusion of oxygen to the metal surface is expected to be markedly affected. The oxygen carried molecules of sodium nitrite is expected to vanish with the increase of temperature and less quantity of inhibitor compare with tests at room temperature is expected to be adsorbed at metal surface.[8]

CONCLUSIONS

1- The inhibitor efficiency found to be markedly dependence on the degree of metal surface finish. Samples ground using smooth grinding paper (1000 grit paper) showed highest Rp value and the inhibitor performance was found to be highest.

2- Ground and corroded samples markedly reduced the performance of sodium nitrite inhibitor. This was found to depend on the degree of metal surface finish.

3- Tests at (70 ± 2° C) markedly reduced the performance of sodium nitrite inhibitor even when tests were conducted on smooth surface finish samples (ground at 1000 grit paper) and highest inhibitor concentration (800 ppm).

REFERENCES

[1] European Federation of Corrosion Inhibitor Working Party,1996. An intensive course in theory and practice of corrosion inhibitor (prepared in cooperation with DECHEMA, Frankfurt, Germany.

[2] *Reviews on Corrosion Inhibitor Science and Technology*. **2**, Edited by A. Raman and P. Labine.

[3] *Engineering Solutions for Corrosion in Oil and Gas Applications*,1989. Proceedings of the, second NACE International Symposium. November 14-17, Milan, Italy, R.N. Parking, Editor.

[4] European Federation of Corrosion publications, November 11th, 1986. *A Working Party, Report on Corrosion Inhibitors*, Published for the European Federation of Corrosion by the Institute of Materials. September

[5] Mercer .A.D, Jenkins. I. R and Rhoades-Brown J. E, 1968 (May). Comparative study of factors influencing the action of corrosion inhibitor for mild steel in neural solution, III.* Sodium Nitrite. *Br. Corros.* J., 3,136-137.

[6] Brasher. Dora M, Reichenberg. D and Mercer. A. D, 1968 (May). Mechanism of action of mixed inhibitive and aggressive anions. *Br. Corros.* J., **3**, 145.

[7] Brasher. Dora M, DE. C. P and Mercer. A. D ,1966 (March). Film growth on mild steel in inhibitive solution. *Br. Corros.* J., **1** .

[8] Mercer. A. D and Jenkins. I. R, 1968 (May). Comparative study of factors influencing the action of corrosion inhibitor for mild steel in neural solution, II. Potassium Chromate. *Br. Corros.* J., **3**, 133.

Petroleum Res. J. Vol. 17 (2005); P. 47–54, 2 Figs.

Overview of Scale Treatment in Oilfield Environments from a Technical Viewpoint

James A. McRae, Catherine J. Strachan and Alex Thornton*

مراجعة عامة لمعالجة الرواسب القشرية في بيئات حقل نفط من الناحية التقنية

جيمس أ. مكري وكثرين ج. ستراكن وألكس تورنتن

تنعكس التحديات المستمرة التي فرضت نفسها بسبب تزايد المشاكل الناتجة من الرواسب القشرية بالحقول النفطية في استمرارية الجهود البحثية المبذولة عالميا والمسخرة في تطوير تقنيات أفضل وأكثر حداثة في مجالي التقليل منه والتحكم فيه.

تتناول هذه الورقة بوجه عام مراجعة الطرق الكفيلة والمستخدمة للحد من مشاكل القشور المترسبة في المعدات النفطية السطحية والأخرى بداخل الآبار المنتجة مع التركيز على سلسلة مختارة من مضادات الترسب القشري المتطورة والمصممة لضمان تدفق النفط باستخدام تقنية بديلة عن التقنيات التقليدية.

لقد تم التعرض للاجابة على الأسئلة المتعلقة بمتى يجب أن تتم المعالجة وبماذا ، خاصة عندما تكون كمية المياه المصاحبة للنفط قليلة وكذلك متى يوقف ضخ مضادات الترسب القشري في عمق البئر وبما يمكن التحكم في الحالات الصعبة (مثل الآبار التي بها تشققات بالصخور الحاوية للنفط أو التي تعطي ضغطا منخفضا عند القاع).

Abstract: *The continuing challenge posed by oilfield scale is most clearly reflected in the significant ongoing global research effort dedicated to developing newer and better technologies for its mitigation and control. This paper provides an overview of the current status of topside and downhole oilfield scale control methodologies, and focuses on a selected series of anti-scaling developments that are designed to provide the oilfield flow assurance engineer with much needed alternatives to 'conventional technologies'. The question of – 'when to squeeze-treat', and 'with what' is addressed with respect to low watercut wells and also, two non-squeeze downhole anti-scaling options are described that can provide scale control in difficult well situations (i.e. fractured completions and wells exhibiting low downhole pressure).*

INTRODUCTION

Oilfield scaling is ranked amongst the top three key flow assurance concerns in oil and gas production. If left unchecked, inorganic scale deposition can result in a myriad of production/process problems that often require time consuming and costly intervention to correct[1]. Oilfield operations commonly affected by scaling include;

(i) Drilling and Completions.
(ii) Water Injection (including produced water re-injection).
(iii) Hydrocarbon drainage.
(iv) Process operations.

Scale 'prevention' by means of chemical scale inhibitor application is now the preferred mechanism adopted by the oil industry to address mineral scaling issues. A number of 'Fluid' and 'Flow' modification technologies such as desulphation, filtration/ coagulation and water shut-off have been used by the industry for reducing scale problems, however

* Clariant Oil Service Scotland.

they invariably involve chemical scale inhibitor use at some stage during their specific action to ensure complete control of scale[2,3]. Scale inhibitor application is widely regarded as the most cost-effective solution to the majority of oilfield scaling problems with continuous chemical injection and batch squeeze treatment considered as standard for managing scale in 'topsides' and 'downhole' process scenarios respectively.

The oil industry has become increasingly technologically sophisticated in its pursuit and exploitation of hydrocarbons globally, and this is most clearly demonstrated by the renewed interest in reserves that have hitherto been regarded as potentially geographically and/or geologically challenging[2,4,5]. Much effort has been directed towards the engineering and mechanistic aspects of the hydrocarbon recovery process, particularly towards the latter half of the 20th century. By contrast, it is only relatively recently that the same focus and effort has been accorded to flow assurance challenges associated with brines co-produced during hydrocarbon recovery. Scale related technology has therefore needed to develop quickly to 'catch-up' and meet the increasing demands posed by the rapidly expanding oil industry. The importance of scale technology to the success of the oil industry cannot be overstated particularly for the new generation of challenging well ventures.

This paper discusses general scaling control strategies and touches upon current trends in topsides scaling control. However, the majority of the overview concentrates on downhole scale control using chemical scale inhibitors. The question of – 'when to squeeze-treat', and 'with what' is briefly discussed with respect to low watercut wells in simple well scenarios.

Examples of alternative non-squeeze options are also discussed which are applicable to difficult well situations *i.e.* fractured completions and wells exhibiting low downhole pressure.

MINERAL SCALING

Mixed salt solutions or 'brines' are commonly associated with hydrocarbon bearing formations and will, regardless of the total dissolved salt content, be clear and continuous under the equilibrium conditions existing in the undisturbed reservoir. On first contact and throughout subsequent development and exploitation, the brine equilibrium will change, resulting in an increased potential for the more sparingly soluble salts to destabilise and phase separate out of solution. The increased scaling potential is largely dependent upon the formation waters salt loading and the physical changes that the system has experienced. In the majority of formation water self-scaling cases, calcite ($CaCO_3$) is usually the dominant scaling species, and can occur from downhole to topside depending upon the bubble point of the system.

Ingress and co-production of a sulphate rich brine-seawater with reservoir formation water during hydrocarbon recovery can result in formation sulphate scales of alkaline earth metals. The most commonly encountered scales are. barite ($BaSO_4$), celestite ($SrSO_4$), anhydrite ($CaSO_4$) or gypsum ($CaSO_4.2H_2O$). Sulphate scales present greater challenges as their sparingly soluble nature makes them more difficult to control and remove once formed compared to carbonate scales. Barite scale is regarded as being particularly difficult because of its tendency to form rapidly at most temperatures, and once formed, is extremely difficult to remove[6]. In complex brine mixtures; no single scale type occurs exclusively, and therefore, multiple scaling potentials have to be considered. Scale precipitation is promoted by the relative abundance of nucleation sites. The sites do not necessarily need to be scale crystals and can be formation fines, asphaltene or corrosion particulates.

Although oilfield scale is generally thought of as primarily carbonates and/or sulphates of the alkaline earth metals calcium, strontium and barium, complex salts of iron such as the sulphides, hydrous oxides and carbonates may also form as solid deposits, resulting in similar fouling problems for oilfield operating systems[7].

SCALE CONTROL

Prevention is better than cure' is particularly relevant to inorganic scaling in the oilfield environment. At the forefront of prevention are scale inhibitors chemicals[8]. Scale inhibitors fall into two basic categories, the organophosphonates such as DTPMPA and water-soluble polymers such as PCA. New inhibitors include sophisticated molecules that exhibit anti-scaling properties common to both generic types[9]. Inorganic phosphates are also used by the industry and are considered effective for calcium carbonate scale inhibition. Their use is however limited by their tendency to hydrolyse in aqueous

media to form orthophosphates that effectively have no appreciable anti-scaling capability.

Scale inhibitors function by interfering with scale crystal growth. Some molecules act primarily as crystal nucleation inhibitors where endothermic adsorption on nucleating crystal embryos causes an increase in the crystal radius required for further crystallisation and hence inhibition of the process. Others irreversibly adsorb at active crystal growth sites that effectively 'snuffs-out' further growth at these locations on the growing scale crystal resulting in growth inhibition. Inhibitors act in non-stoichometric proportions compared to the concentration of scaling ions present. Successful inhibitors are those that maintain crystal growth suppression when present even at very low concentration for extended periods of time and across the targeted physical conditions. The number and diversity of unique oilfield scaling scenarios is most clearly demonstrated by the large number of commercially available scale inhibitors.

Topsides

Topside facilities receive raw unprocessed well fluids from a number of sources that are firstly merged before entering the topsides system for processing. Scaling occurs when brines co-produced with hydrocarbons experience changes in fluid composition (through mixing), pH, temperature and pressure. Topsides processing systems, because of their very function, are prone to scaling and therefore require continuous scale inhibitor chemical application to ensure control across the plant. Although the mechanical action of process systems can create scaling hotspots throughout the system, topsides scale is generally regarded as being simpler to control than downhole scale, mainly because of the high accessibility offered by the majority of surface installations.

Prior to deployment, topside scale inhibitor is required to fulfil certain selection criteria;

(i) The chemical should be effective at low concentration for the control of water based scales specific to that system and its operational conditions.

(ii) The chemical should be benign to the system, its flowing components and any other process chemical additives used in the process.

(iii) The chemical should be readily monitorable via simple yet robust analytical techniques.

(iv) The chemical should be environmentally friendly.

Topsides Continuous Injection

In the simplest case, an onshore or offshore production installation manifolds received fluids prior to primary dehydration for bulk water removal. Incoming waters may contain scale inhibitor from. upstream squeeze operations, however additional dosing of topside inhibitor is usually necessary to provide complete control across the process system. Dosing is usually performed at the 'christmas tree' of source wells to allow sufficient mixing time prior to dosed stream merging with other fluid streams in the production manifold. In some cases additional scale inhibitor dosing is required upstream of scaling 'hotspots' where an increased scaling tendency is evident, usually caused by a specific process system action *i.e* heating/cooling of the fluid stream, low or stagnant flow regimes and also degassification systems.

Downhole Continuous Injection

Topsides scale protection can also be provided by downhole chemical injection. Although expensive to install and maintain, the downhole injection system will provide scale cover for all tubing and upstream equipment (xmas trees, safety valves, gas-lift interfaces) as well as the topsides process system tubing and interfaces. The most frequently encountered issue with downhole chemical injection systems is system failure caused by a blocked or crimped umbilical or fouled inoperable injection nozzle. Remedial interventions to correct downwell faults are expensive and can be technically challenging due to the relative inaccessibility of the downwell environment. An alternative route to deploying scale inhibitor downhole is via the well gas-lift system. For wells that have gas-lift but no downhole chemical injection system installed, this can provide a cost-effective method of deploying scale inhibitor into tubing without the expense of retro-fitting injection equipment. Gas-lift scale inhibitors are specially formulated to exist unaffected within the unique conditions that exist within the gas-lift environment[10].

Deep Downhole Continuous Injection

Deep downhole chemical injection allows scale inhibitor to be deployed at the near wellbore perforation face for scale control in situations where conventional near-wellbore scale protection methods are impractical *i.e* squeeze treating high demand

wells[11]. Deep application technology is still in its infancy but may offer a realistic alternative to some of the more technically challenging scaling environments.

Downhole

Downhole scaling presents by far the greatest scaling challenges within the oil industry because of,

(i) Wellbores and near wellbore areas are relatively inaccessible.

(ii) Wellbore formations are usually complex and petrophysically heterogeneous in nature.

(iii) Routine wellbore surveillance tends to be given low status on the list of well intervention priorities.

(iv) Downhole conditions are usually significantly harsher than those experienced in any other part of the production system.

SCALE SQUEEZE INHIBITORS

Scale inhibitor chemicals are routinely used downhole wherever the risk of scale damage is predicted or suspected (from a field history perspective). For downhole application, scale inhibitors are routinely batch deployed via 'squeeze-treatment' into the near wellbore formation of the target well to achieve control of scale across the near-wellbore perforations upwards. Squeeze designs are optimised to achieve the longest 'safe' squeeze lifetime whilst minimising the well downtime. Squeeze chemicals therefore have to be retained within the reservoir and then returned at sufficient concentration within the normal produced fluids to prevent scale – for as long a time period as possible. Squeeze treatments have historically relied upon the scale inhibitor chemicals ability to interact with the formation surface through adsorption to enable the chemical to be retained within the reservoir. Precipitation type squeeze treatments provide an alternative method of retaining aqueous treatments within the reservoir by the controlled phase separation of an inhibitor-salt complex within the near wellbore formation. The precipitation squeezes can provide squeeze lifetime extension of up to three times depending upon the system anti-scaling requirements compared to its conventional adsorption squeeze analogue. Squeeze lifetime extension can be improved for both adsorption and precipitation type treatments by application of squeeze lifetime extension chemicals as part of the squeeze treatment package[12].

Squeeze Treatments

A squeeze treatment generally involves stopping production from the well concerned, followed by application of a concentrated solution of scale inhibitor that is pumped into the well and oveflushed out from the wellbore 5-25ft depending upon the perforated interval. After a shut-in period of 6-24 hours, production is resumed and the scale inhibitor leaches back into produced fluids, providing protection against scale formation until the scale inhibitor is exhausted. The performance of the squeeze treatment is usually performed via monitoring for scaling ions and scale inhibitor residuals in returning well fluids. Successful treatments are those regarded as achieving their designed lifetimes.

Squeeze Design Optimisation

In order to optimise the field performance of a squeeze chemical, the inhibitor must first be deployed correctly in the field, or coreflood tested under field conditions. Collected inhibitor residuals return data can then be used to derive a mathematical algorithm based upon conventional fluid-surface isotherms which can be used to model and sense-test new squeeze treatment designs.

Low Watercut Wells -When to Squeeze?

Low watercut wells pose unique scaling problems when their waters exhibit a significant scaling potential.

Conventional aqueous treatments are to be avoided because of the increased risk of water related formation damage, therefore non-aqueous alternatives have to be considered to avoid unwanted emulsification, wettability and water stimulation problems[13,14]. Low-watercut is commonly regarded as <5% of total production, however this interpretation can be very much operator specific. Equally important is the total produced fluid volume; if this is low *i.e.* 500bfpd then the potential precipitating mass will be restricted by the low volume of aqueous fluid, see Table 1. Ideally, scale protection should be available at first production to minimise the possibility of any scale deposition and build-up occurring downhole. This can be achieved by pre-emptively squeezing the 'dry' well with a suitable

non-aqueous scale inhibitor, or by deploying non-squeezing scale inhibition options in the well if its completion permits.

Table 1. When to squeeze for low watercut wells

Water (%)	Scaling	BFPD tendency	Squeeze ?	Comments
< 5	Low	500	No	Monitor scaling ions for changes
< 5	Low	5000	No	Monitor scaling ions for changes
< 5	Medium	500	Yes	Monitor scaling ions for changes
< 5	Medium	5000	Yes	Consider pre-emptive squeeze
< 5	Harsh	500	Yes	Consider pre-emptive squeeze
< 5	Harsh	5000	Yes	Consider pre-emptive squeeze

A number of pre-emptive non-aqueous squeezing options are available, including oil soluble, oil miscible, oil dispersed and oil continuous scale inhibitors. Selection of a suitable chemical and deployment package for squeeze treating the wells is best performed by coreflood testing the candidate using representative field core under field conditions to assess for possible formation damage issues.

For watercuts >5%, the range of squeeze treatment technologies increases with the increasing level of water breakthrough. From 5-25%, alternative squeeze technologies such as emulsified scale inhibitors and tailored aqueous based treatments combined with wettability modifying agents can be deployed to provide scale control downhole while minimising the impact on production and the formation.

Squeezing – New Alternatives

Future oilfield developments are most likely to be located in the more remote challenging environments such as deep water developments, high temperature, high pressure formations and remote subsea completed wells. Scale inhibitor research and development is focussed on improving the efficiency of scale inhibitors and enhancing deployment technology to minimise the number of well interventions required to maintain scale control. The existing older technologies are constantly being optimised and improved while newer scale inhibitor technologies are under evaluation that are designed to optimise the placement of scale inhibitors in critical locations within the near wellbore formation to enhance the treatment lifetime.

Emulsified Squeeze Inhibitors

A number of emulsified scale inhibitors are currently available in the marketplace for use in squeeze treatments. Invert emulsions are generally water-in-oil emulsions where the water component contains the scale inhibitor. The emulsion package is considered as a non-aqueous package that allows oil continuity during treatment[15,16,17]. The emulsified chemicals are relatively benign to the formation whilst also achieving deeper penetration of the treatment into the formation to improve flowback character compared to their conventional aqueous based analogues. Improved retention within the formation has led to increased squeeze lifetimes.

OIL DISPERSED/OIL SOLUBLE/CRUDE OIL SOLUBLE SCALE INHIBITORS

Oil based scale inhibitors are directly applicable to low watercut wells that express significant scaling potential and also wells that suffer poor restart or that are water sensitive. The majority of commercial 'oil soluble/oil dispersed/oil continuous products still use aqueous based inhibitors in their formulation which makes them less amenable to deployment in formations that are known to be water sensitive[18,19,20]. More recently, new crude oil soluble inhibitor products have been made available that contain absolutely no aqueous based components in their formulation which should provide additional benefits when squeeze treating formations that are extremely water sensitive[21].

Impregnated Proppant

Well production can be stimulated through artificially fracturing the formation around the wellbore to increase the surface area through which hydrocarbons can enter the well.

Hydraulic fracturing is a temporary phenomenon that is maintained as long as the applied pressure is maintained. Small, strong ceramic beads or 'proppant' are injected during the hydraulic fracturing process to maintain the fracture after the well is returned to production. In most fracturing operations, large quantities of proppant are used per job, although not all proppant remains within the reservoir on back production. Ceramic proppant beads are porous and this porosity can be utilised to store solid scale inhibitor without impacting upon the mechanical integrity of the beads[22, 23].

Fractured wells are notoriously difficult to squeeze effectively, therefore application of impregnated proppant provides a useful alternative to squeeze treating wells to maintain scale control, see Figure 1. The entrapped solid scale inhibitor slowly dissolves into the aqueous phase across a long period of time, providing scale control in excess of that achievable through conventional aqueous based scale inhibitor squeeze chemistries and technologies. The technique is versatile and the nature of the scale inhibitor can be changed to reflect the demands of the targeted downhole scaling environment. The beads are pumped as a fraction of the normal proppant load (typically 5-20wt%) and start to release scale inhibitor when they come into in contact with well water. Impregnated proppant technology is particularly important for treating fractured low watercut wells as the inhibitor is in place and ready for the onset of water production. Scale control will ensue as long as the inhibitor releases above the required Minimum Inhibitory Concentration (MIC).

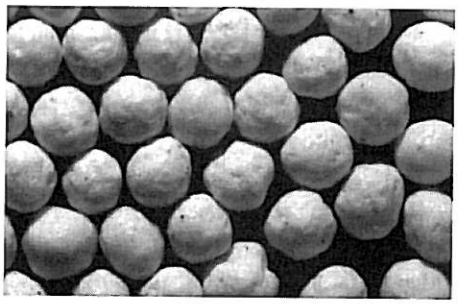


Fig. 1. Impregnated proppant beads.

Case #1

A North Sea oil well was producing 5700 bbl oil per day dry that dramatically reduced to 150 bbl per day after water breakthrough. The impairment was caused by the build up of mineral scale across the near wellbore perforations. Re-perforation did not provide the oil production increase that was expected, therefore a hydraulic fracture treatment was performed incorporating impregnated proppant to provide downhole scale control. Well production increased to 3072 BOPD, before averaging out at approximately 2600 BOPD nine months after fracturing.

Solid Encapsulated Scale Inhibitor System

Wells that have low operating pressure and/or water sensitive formations are notoriously difficult to treat using conventional scale mitigation technologies. Although non-aqueous and emulsified scale inhibitors can be used in some instances, it is considered preferable not to load the near wellbore formation with tons of injected cold fluid. If the well is fractured then repeat application with impregnated proppant should be considered, however for non fractured types or wells using submersible pumps, micro-encapsulated scale inhibitor solid particulates can be used[24,25]. The technique is most suited to vertical wells but can also be applied to deviated wells and deployed downhole in screens and inserts. The solid scale inhibitor material can also be deployed using hanging baskets or as pre-soak treatments for wash water. The weighted polymer composite comprises solid scale inhibitor (25-30wt%) encapsulated in a degradable matrix. The material acts on contact with aqueous fluid forming an inhibitor diffusion gradient from the sump to the closest water producing perforation. The well is effectively protected by the 'first-order' release of scale inhibitor into the flowing fluid stream.

Case #2

In 1999, a solid scale inhibitor treatment was targeted for a low-pressure oil producing well, where conventional aqueous squeeze treatment was considered impractical. The field had been producing oil since 1987, with seawater injection used for reservoir support since 1988. By 1999 the reservoir pressure had declined almost to an equilibrium level and no gas-lift system was in place to aid start-up and production.

The well hydrostatic head disallowed usage of conventional water based squeeze treatments to control a moderate calcium/strontium carbonate and

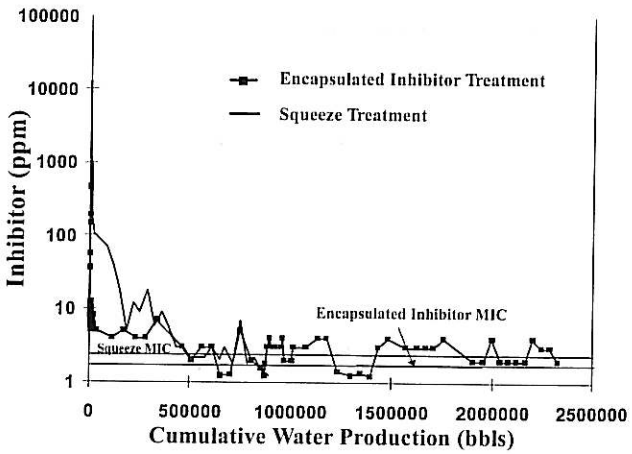


Fig. 2. Comparison of produced water volume treated by a micro- encapsulated particulate treatment and a conventional aqueous squeeze treatment performed on the same well.

barium sulphate scaling potential. Encapsulated scale inhibitor was deployed provided approximately three-times the conventional squeeze lifetime for the well with 2.5 MMbbls of water protected above MIC compared to 0.8MMbbls protected using conventional squeeze treatment technology, see Figure 2.

The encapsulated inhibitor deployment also provided significant additional benefits with respect well downtime and also ease of restarting post-treatment. From a gross costing perspective, the encapsulated treatment cost less than one third of the conventional treatment performed previously on the same well.

CONCLUSIONS

- Scale inhibitor technology has advanced rapidly over the last 15 years and is now matching the ever-increasing technical challenges posed by the oil and gas industry.
- The recognised industry standard method for scale control in oilfield systems is by application of chemical scale inhibitors.
- Many non-scale inhibitor technologies have been and are used in the industry to mitigate problems associated with scale, however in most cases scale-inhibitor application is needed to 'polish' the process.
- A range of alternative squeeze chemicals and technologies are available for controlling scale in routine and also non-routine down-well circumstances
- Low watercut wells often present significant unique challenges with respect to squeeze treatment selection and application.
- The issue of 'when to squeeze a well' can be answered by reviewing the potential risks to the well and by also reviewing the range of squeeze chemical candidates available for the conditions
- Newer alternative non-squeezing chemical options include Deep Down Chemical Injection, micro-encapsulated scale inhibitor particulates and impregnated proppant beads.

REFERENCES

[1] Hinrichsen, C.J., 1998. Preventing scale deposition in oil production facilities: an industry review. Paper No.61 presented at NACE Corrosion 98, Houston, Texas.

[2] Vu, V.K., Hurtevent, C and Davis, R.A., 2001. Eliminating the need for scale inhibition treatments for Elf Exploration Angola's Girassol Field. paper **SPE** 60220 presented at the SPE 3rd International Symposium on Oilfield Scale, Aberdeen, Scotland, 30-31 January.

[3] Hardy, J.A., and Simm, I., 1996(2 Dec.). Low sulfate seawater mitigates barite scale. *Oil and Gas Journal*, 58-63.

[4] *Deepwater Technology Supplement to World Oil*, 2000 (August). Gulf Publishing.

[5] Rosario, F.F. and Bezerra, M.C.M., 2001 (January). Scale potential of a deep water field – water characterisation and scaling assessment: Paper **SPE** 68332 presented at the SPE 3rd International Symposium on Oilfield Scale, Aberdeen, Scotland, 30-31.

[6] Mendoza, A., Graham, G.M. and Sorbie, K.S., 1999. Sulphate scale dissolution: examination of the factors controlling the effectivness of EDTA and DTPA based scale dissolvers and their comparitive effectiveness against different sulphate minerals: 10th NIF International Oil Field Chemical Symposium, Fagerness, Norway.

[7] Metcalf, A.S., and De Vine, C.S., 2003. Mechanisms of iron scale formation: Paper **SPE** 80388 presented at the SPE Oilfield Scale Symposium, Aberdeen, Scotland.

[8] Graham, G.M., Jordan, M.M., and Sorbie, K.S., 1997. How scale inhibitors work and how this affects test methodology: 3rd International Conference on Advances in Solving Oilfield Scaling, organised by IBC Technical Services Ltd., Aberdeen, Scotland, 22-23 January.

[9] Bourne, H.M., Buckley, A.S., Fleming, N., Hansen, A-M., and Strachan, C.J., 2001. Development of an ecofriendly scale inhibitor for harsh scaling environments. 12th NIF International Oil Field Chemical Symposium, Geilo, Norway.

[10] Cowie, L.G., Ravenscroft, P., Heath, S., and Bourne, H.M., 1999. Delivering chemicals to production wells via gas lift – where are we? 1st SPE Symposium on Oilfield Scale, Field Applications and Novel Solutions, Aberdeen, Scotland, 27-28 January .

[11] Webb, P., *et al.*, 2003. Deep downhole chemical injection development and field application on BP Miller. BP internal Publication.

[12] Collins, I.R., Cowie, L.G., Nicol, M., and Stewart, N.J., The field application of a scale inhibitor squeeze enhancing additive. **SPE** paper 38765.

[13] Graham, G.M., Hill, P.H., Sorbie, K.S., Carbonne, L. and Stott, L.,1999. The mechanism of formation damage and recovery following chemical squeeze application in low permeability water sensitive

reservoirs: 10th NIF International Oil Field Chemical Symposium, Fagerness, Norway, 28 February- 3 March.

[14] Bourne, H.M., Buckley, A.S., Fleming, N., Spark, A.S., Patey, I., Carbonne, L. and Stott, L., 1999. A mechanistic investigation of the Dunbar scale challenge – the use of cryogenic SEM to determine wettability alteration: 1st SPE Symposium on Oilfield Scale: Field Application and Novel Solutions, Aberdeen, Scotland, 27-28 January.

[15] Collins, I.R., Jordan, M.M., Feasey, N. and Williams, G.D., 2001. The development of emulsion-based production chemical deployment systems: paper **SPE** 65026 presented at the SPE Symposium on Oilfield Chemistry, Houston, Texas, 13-16 February.

[16] Nasr-El-Din, H.A., Saiari, H.A., Hashem, M.K., and Bitar, G., 2003 (January). Optimisation of a novel emulsified scale inhibitor sytem to mitigate calcium carbonate scale in a sandstone reservoir in Saudi Arabia. **SPE** 80389 presented at the **SPE** Oilfield Scale Symposium, Aberdeen, Scotland.

[17] Smith, R.N., Lawless, T.A., Bourne, H.M., Brunger, A., Nicoll, D., Hurtevent, C., and Ainsworth, A., 2000 (January). Planning and execution of a field trial utilising new invert emulsion squeeze technology, paper **SPE** 60210 presented at the SPE 2nd International Symposium on Oilfield Scale, Aberdeen, Scotland.

[18] Heath, S.M., Thornton, A.R., Strachan, C.J., McClure, R., Williams, G.D., Wylde, G., and Hansen, A-M., 2003 (March). Development of an environmentally friendly non-aqueous scale inhibitor for harsh scaling environments. NIF Oil Field Chemistry Symposium, Geilo.

[19] Graham G.M., Gyani A., Jordan M.M., Strachan C., McClure R., Littlehales I.J., Fitzgerald A., 2002 (January). Selection and application of a non-damaging scale inhibitor package for pre-emptive squeeze in Mungo production wells , 2002. Paper SPE 74665 presented at the SPE 4th International Symposium on Oilfield Scale, Aberdeen, Scotland.

[20] Wat, R.M.S., Maclean, A.F., Barber, L., Wallace, M., and Jones, T.L., 1999. Oil soluble scale inhibitor (OSI) squeeze treatment – the first North Sea case history. Proceedings of; SPE Oilfield Scale Symposium, Aberdeen, January .

[21] Wylde, J.J., 2004. The advent of a truly oil soluble scale squeeze inhibitor. Accepted for NACE 2004, New Orleans.

[22] Webb, P.J.C., Nistad, T.A., Knapstad, B., Ravenscroft, P.D., and Collins, I.R., 1999. Advantages of a new chemical delivery system for fractured and gravel-packed wells.SPE Prod & Facilities, **14** (3), 210-218.

[23] Norris, M., Perez, D., Bourne, H.M., and Heath, S.M., 2001. Maintaining fracture performance through active scale control. **SPE** 68300 presented at the 3rd International Symposium on Oilfield Scale, Aberdeen, Scotland, 30-31 January.

[24] Collins, I.R., 1997. Scale inhibitor impregnated particles – field applications 3rd International Conference on Solving Oilfield Scaling, organised by IBC Technical Services Ltd, Aberdeen, 22-23 January.

[25] Bourne, H.M., Heath, S.M., McKay, S., Fraser, J., Stott, L., and Muller, S., 2000. Effective treatment of subsea wells with a solid scale inhibitor system. Paper SPE 60207 presented at the 2nd International Symposium on Oilfield Scale, Aberdeen, Scotland, 26-27 January.

Petroleum Res. J. Vol. 17 (2005); P. 55–58, 4 Figs.

Scale Inhibitor Evaluation and Optimization

Salem Abuoun*, Said Alforjani*, Radia Sola*, and Miloud Alarabi**

تقييم موانع الترسيب المستخدمة في الحقول النفطية

سالم أبوعون وسعيد الفرجاني وراضية صولة وميلود العربي

تعتبر عمليات الاسترداد الإضافي من العمليات المهمة في مجال استخراج النفط في الحقول المنتجة محلياً، وتشمل هذه العملية حقن طبقة المكمن المنتجة للنفط بالمياه من اجل المحافظة على ضغطه. غير أن عدم تطابق هذه المياه مع مياه التكاوين قد يؤدي إلى ترسيب العديد من مكوناتها على هيئة قشور وترسبات مثل كربونات الكالسيوم وكبريتات الكالسيوم وكبريتات الباريوم وكبريتات السترانشيوم والتي تؤدي إلى انسداد بعض أنابيب إنتاج النفط وتلف في بعض المعدات مثل المضخات وصمامات الأمان.

في هذه الدراسة تم إجراء إختبارات معملية للعديد من موانع الترسيب المستخدمة محليا لاختيار الأمثل منها من حيث الأداء والكفاءة وفق الطرق القياسية، وأيضاً تم استخدام بعض النماذج الرياضية لحساب وتقدير إمكانية تكون هذه الترسبات ومقارنتها بالنتائج المعملية.

Abstract: *Secondary oil recovery represents a major part of oil production in many local oilfields. It involves injection of a source water to maintain the reservoir pressure. The source water will eventually mixed with formation water as it breakthrough to production well. Mixing of incompatible brines leads to precipitation of various types of mineral scaling compounds such as barium sulfate, strontium sulfate, calcium sulfate or calcium carbonate. This scale deposits at formation face, production tubing, subsurface valves, perforation may restrict fluids flow that result in production rate curtailment. A laboratory work is currently underway to set up a standard procedure for scale inhibitor selection. This paper presents the result of evaluating different types of commercially available scale inhibitors intended for use under down hole and surface production facilities conditions. In addition, a computer scaling modeling is performed to asses the compatibility of injection and formation brines at different ratios and various temperature and pressure conditions.*

INTRODUCTION

Most water handling problems in oil and gas production arise from the fact that water is an excellent solvent [1]. In oilfield both source water and formation water contain considerable quantities of dissolved solids, suspended solids and dissolved gases. As conditions of temperature and pressure change, many dissolving compounds may become insoluble to some degree, precipitate from water and may form scale.

Two major types of scales are commonly encountered in water handling operations [2], these being carbonate and sulfate based scales. The formation of carbonate scales (calcite ($CaCO_3$) is usually associated with changes in pressure,

* Petroleum Research Centre, P.O. BOX 6431, Tripoli, Libya.
** Chemical Engineering Department, Al Fateh University, Tripoli, Libya.

temperature, pH, and dissolved CO_2, as water passes from surface into the formation or from formation to surface facilities. Sulphate scale formation [gypsum ($CaSO_4.2H_2O$), anhydrite ($CaSO_4$), celestine ($SrSO_4$) or barite ($BaSO_4$)] is often associated with potential incompatibilities between formation and injection water and to a lesser extent on temperature and pressure. The forecast of these incompatibility effects on the future oilfield operation should cover type, extent and location of all future location of all future damage due to chemical incompatibility problems.

The usual method of scale prevention is to apply scale inhibitor that generally fall into one of the four main classes polyphosphates, phosphate esters, phosphonates and polymers [3] .These four types are known as threshold chemicals that inhibit scale at a concentration well below equimolar amounts. Each type of chemical has a certain application subject to laboratory and field trials before continuous application. For an effective scale control program, the inhibitor should be present at all times in the water being treated. Furthermore, it is important that the inhibitor should be added to the system at a location upstream of the point where scale deposition starts to occur. Different types of commercial scale inhibitors are being tested under static and at reservoir conditions. This paper presents part of scale inhibitor evaluation intended to cover most of scale inhibitors used in local oil fields. Also, in house software program is developed to asses and predict the self scaling or incompatible mixing of formation and injection water. This prediction covers the type extent and location of all expected scale deposition.

Scale Inhibitor Evaluation

To be suitable for scale inhibition [4], an inhibitor must:

- Inhibit scale formation at low concentration.
- Be stable at reservoir conditions.
- Be compatible with injection and formation waters /and all types of chemicals used in oilfields.
- Have a reasonable solubility at reservoir conditions.
- Be measurable quantitatively at low concentration.
- Have low toxicity and high biodegradability.
- Have low cost.

These requirements formed the bases for screening criteria and tests. Four commercial scale inhibitors labeled as A,B,C and D (Table 1, and reference 5) are evaluated according to the procedure outlined in NACE Standard (NACE – TM0374-2001) (test method and laboratory screening tests to determine the ability of scale inhibitors to prevent the precipitation of calcium sulfate and calcium carbonate from solution)[5]. Synthetic supersaturated solutions that represent actual injection and formation waters are used since no meaningful results can be obtained using oilfield brines.

The main objective of this test is to screen scale inhibitors under accelerated condition and provide relative performance rankings. Any product fail this test will be eliminated for further testing. The effectiveness of each product is measured by its ability to keep the calcium ions in the solution.

Table 1. Scale inhibitors tested.

Scale inhibitors	Chemical composition
A	Blend of phosphonates and polymer
B	Neutralised sodium salt of phosphonate
C	Phosphate ester
D	Organic phosphonate

RESULTS AND DISCUSION

1. Scale Inhibitor Evaluation Test

Tables 2 and 3 show the results of these tests. The percentage inhibition (m) was calculated according to:

$$m = \frac{C - C_e}{C_o - C_e} \times 100$$

Table 2. Brine composition.

Ion	Formation water mg/l	Injection water mg/l
K^+	437	90
Mg^{+2}	950	130
Ca^{+2}	8940	450
Sr^{+2}	383	10
Ba^{+2}	1.3	0.2
Na^+	26133	1000
Cl^-	56733	1800
Br^-	401	0.0
$(HCO_3)^-$	196	756
$(SO_4)^{-2}$	605	757

Table 3. Calcium sulfate percent inhibition %.

Concentration/ Scale inhibitor	1 mg/l	3 mg/l	5mg/l	10mg/l	20 mg/l
A	35.48	83.87	87.09	100	100
B	75.92	77.77	81.85	83.33	83.33
C	82.75	90.52	93.10	93.10	93.10
D	68.42	89.47	92.98	97.37	97.37

Where: C_e is the equilibrium divalent cation concentration in the absence of inhibitor
C_o is the initial divalent cation concentration.

The same results are also shown graphically for better comparison in Figures 1 and 2. For most oilfield application, a minimum effective dosage for threshold inhibitor is in the range of 1 – 5 mg/l which is sufficient to prevent mineral scaling. Therefore; all products are acceptable for preventing sulfate scaling. However, only inhibitor C is superior to the others to inhibit calcium carbonate.

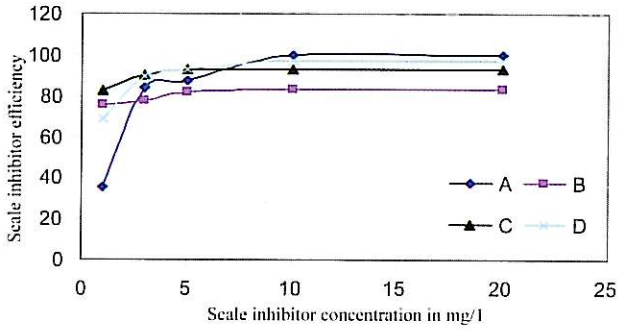


Fig. 1. Percentage inhibition of ($CaSO_4$) from static test.

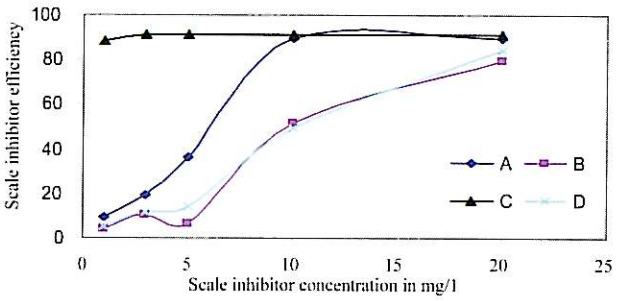


Fig. 2. Percentage inhibition of ($CaCO_3$) from static test.

2. Computer Scale Prediction

In house developed prediction model , based on Odd and Tomson method[6], has been carried-out for one oilfield to asses the self- scaling or incompatibility mixing, at three locations (down hole ,wellhead and manifold). All the relevant data, water composition and gas composition of brine at equilibrium in the reservoir are considered. The data is shown in Table 2. Effects of the pressure and temperature changes associated with the production, and the resulting changes in equilibrium composition are modeled. In this manner potential scaling problems and the driving forces for scale formation are identified. The saturation index (SI) is a measure of scaling tendency. However, if the sign is positive, the brine has a scaling potential, a negative sign indicates the brine is under- saturated.

Figures 3 and 4 illustrate the predicted calcium carbonate and calcium sulfate saturation index as the source water (injection water) mixes with formation water at bottom hole, well head and manifold conditions. The results indicate that calcite scaling is likely at well head and manifold. This is due to reduction in pressure, evolution of CO_2 and increase in pH of the brine. The calcium sulfate scaling is unlikely under the same condition at the three locations.

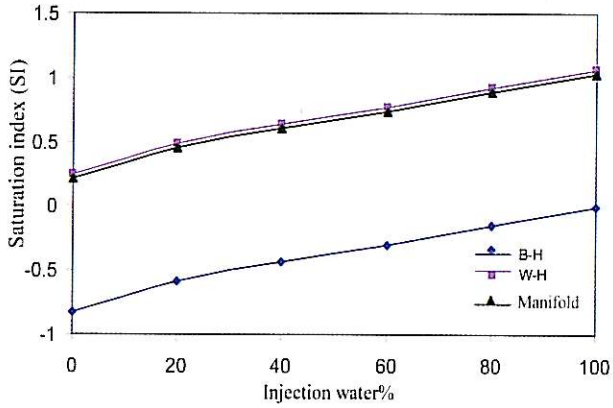


Fig. 3. Calcium carbonate scaling tendency.

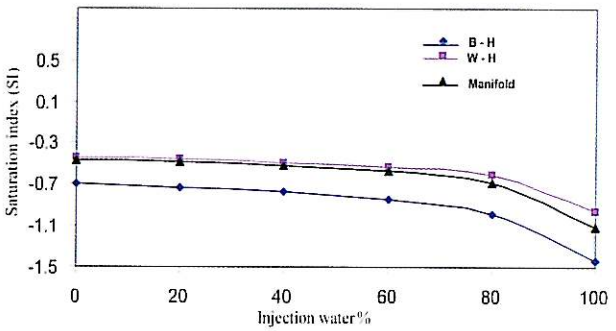


Fig. 4. Calcium sulfate scaling tendency.

CONCLUSIONS

Laboratory static test NACE standard procedure was followed to evaluate the performance of four candidate scale inhibitors labeled A, B, C, and D intended to be used in local oilfields. All four products are acceptable in preventing calcium sulfate while only product C is acceptable for calcium carbonate inhibition. The use of computer model can greatly aid in selection and optimization of scale inhibitors for downhole or surface application. The second phase of the scale inhibition tests will focus on evaluating these products under dynamic conditions (Table 4).

Table 4. Calcium carbonate percent inhibition %.

Concentration/ Scale inhibitor	1 mg/l	3 mg/l	5mg/l	10mg/l	20 mg/l
A	9.09	19.48	36.36	89.61	89.61
B	3.85	10.26	6.41	51.28	79.49
C	88.43	91.16	91.16	91.16	91.16
D	5.19	11.69	14.29	49.35	84.42

ACKNOWLEDGEMENT

We are indebted to PRC for permission to purplish this paper; we also thank all who participated in part of the chemical analyses.

REFERENCES

[1] Cown J.C. and Weintritt D.J., 1976. *Water Formed Scale Deposits*, Gulf Publishing Company (Houston)

[2] Patton C., 1998. *Applied Water Technology*. Campell series.

[3] Hinrichsen .C.J, 1998. Preventing scale deposits in oil production facilities, an industry review, (Houston, TX: NASE International), paper No.61.

[4] Duccini. Y., 1997. High performance oil field scale inhibitors, (Houston, TX: NASE International), paper No.169.

[5] NACE Standard Test Method, 1997. Laboratory Screening Tests to Determine the Ability Of Scale Inhibitors to Prevent the Precipitation Of Calcium Sulfate and Calcium Carbonate From Solution (For Oil and Gas Production Systems) , NASE Standard TM0197-97 , Item No. 21228, (Houston , TX : NASE International).

[6] Oddo. J.E and Tomson. M.T, 1994 (Feb.). Why scale forms in the oilfield and methods to predict it, (SPE Production & Facilities), 47-54.

Petroleum Res. J. Vol. 17 (2005); P. 59-66, 15 Figs.

Microbial Prevention of Wax Deposition During Transportation and Production of Crude Oil

Asma Attomi, I.EL Musrati, B. EL Gammoudi* and M. EL Behlil**

منع ترسب الشمع أثناء إنتاج ونقل النفط الخام بواسطة الأحياء الدقيقة

أسماء التومي وعزالدين المصراتي وبسام القمودي ومحمد البهيليل

يشكل الشمع والترسب البارافيني أحد المشاكل الحادة بحقول النفط المنتجة للنفط البارافيني. عليه تم دراسة هذه المشكلة بواسطة المعالجة الحيوية التي تعتمد على فعالية الأحياء الدقيقة المستوطنة طبيعيا بالبيئات النفطية المحلية ، حيث برهنت الدراسات السابقة على تأثير هذه الكائنات كبديل للطرق الكيميائية التقليدية وذلك لمنع وإزالة ترسب الشمع بمعدات وخطوط أنابيب النفط.

تم في هذه الدراسة عمليا عزل عدة سلالات بكتيرية من ترسبات بحرية ملوثة بالمشتقات النفطية ، وقد أظهرت هذه العزلات بوضوح قدرتها المتميزة على إفراز مركبات مصاحبة لنموها من خلال التكسير الحيوي للسلسلة الهيدروكربونية على هيئة جزئيات حيوية لها خاصية عالية في خفض التوتر والشد السطحيين بين الطبقات السائلة والصلبة مما يساعد المواد الشمعية على المزج والانتشار في الماء وغيره من السوائل الأخرى.

أجريت اختبارات تجريبية على معدلات نمو البكتيريا ودرجة ثبات المستحلب والتكسير الحيوي عن طريق التحاليل باستخدام جهاز الغازكروموتوجراف لخامة حقل السرير قبل وبعد المعالجة الحيوية . ولقد أظهرت النتائج أن التكسير الجزئي قد قلل من المحتوى البارافيني للخامات الثقيلة وزاد من المركبات الهيدروكربونية ذات السلاسل القصيرة خاصة من الالكينات العادية ، كما تم بنجاح عزل البكتيريا المسؤولة عن هذه التغيرات من البيئة المحلية وأعطيت الأسماء $PRCWB_1$, E_1, A1, B_2 هذا وسوف يتم اختبار تأثير هذه العزلات على عدة أنواع من الخامات البارافينية المحلية لغرض توضيح هذه المعطيات ودراسة إمكانية تطبيقها حقليا لمراقبة الترسبات البارافينية في الأنابيب والصهاريج النفطية.

Abstract: *One of the most severe problems at any oil field producing paraffin oils is the wax content and paraffin deposition. The microbial treatment, which is based on the activity of the naturally occurring selected isolated bacteria, proved to be an effective alternative method to the conventional chemical methods in preventing and removing wax deposition in oil field facilities and pipelines.*

Various bacterial species were isolated from different local sea water sediments contaminated by petroleum hydrocarbons. The isolated consortia were found to have the ability of producing biosurfactant in the form of biological molecules. The produced biosurfactant showed higher surface activities, capable of reducing surface and interfacial tension at the interfaces between liquids and solids. This phenomenon allows the mixing and dispersion in water and other liquids.

Experimental tests of specific growth rate (μ_{max}), emulsification stability and degradation strategies with G.C assay for Sarir crude oil were

* Petroleum Research Centre, P.O. Box 6431, Tripoli, Libya.
**Chemical Engineering Department, Al Fateh University.
E-mail: asma_etomi@lycos.com

performed before and after treatment. Results showed that biodegradation had minimized the paraffin contents with further expansion in light fraction of the hydrocarbon sequences, in particular the normal alkanes.

The bacterial isolates, responsible for these changes, were successfully isolated and nominated as PRCW B_1, E_1, A_1 and B_2. These isolates will be further tested on several types of paraffinic crude oils in order to verify such findings and support their application in the field to prevent and control paraffin deposition in oil field facilities and pipelines.

INTRODUCTION

Paraffinic hydrocarbons are organic compounds commonly found in crude oil, consisting of various forms and combinations of aliphatic hydrocarbons, aromatic hydrocarbons, napthenes, and asphaltenes. These different forms and combinations give paraffins their characterizations such as melting point, boiling point, solubility, pour point and cloud point.

Paraffins may be deposited throughout the oil production flow lines starting from the oil well reservoirs up to the storage tanks at the refineries. This deposition is due to the system temperature being lowered below the cloud point, and also due to the change in the crude oil composition. The changes in composition might be due to the evaporation of lighter hydrocarbon fractions (C_1-C_5) present in the crude oil.

According to Rocky Mountain Oil Field Testing Center (1997), there are two mechanisms for paraffin deposition. These mechanisms are the shear dispersion and molecular diffusion. The shear dispersion mechanism describes the relationship between deposition rate and the shear rate. The molecular diffusion mechanisms describe the diffusion process of the paraffinic hydrocarbon to the surfaces due to the temperature gradient of the liquid phase.

Since 1900, several methods were proposed and applied to overcome the problem of paraffin deposition. The injection of chemicals such as solvents and dispersants among the conventional methods is very successful for the control of paraffin precipitation and deposition. However, the chemical treatments proved to be costly and highly toxic (Sadeghazad and Ghaemi, 2003).

During the last decade, microbial remediation was found to be an available alternative method over the conventional methods. Microbial treatment can control paraffin deposition by reducing the length of the paraffin molecule and by producing by-products that act as surfactants and paraffin solvents. The cracking of long chain paraffin will produce an increasing in the API gravity and lowering in the cloud point. The bio-production of surfactants and solvents enables the fluid to solubilize the paraffins and remove paraffin-based skin damage from the well bore (Banat *et al*, 1999).

Remediation of Paraffin Precipitation and Deposition

The microorganisms contributing in the microbial treatment of crude oil, are generally live, naturally occurring, specifically isolated bacteria, and must have the following characteristics (Lazar *et al*, 1999).

- Facultative anaerobic, working in the presence or absence of oxygen.
- Non-pathogenic.
- Contain no sulphate-reducing bacteria or slime-forming bacteria.
- Not genetically altered.
- Water based and environmentally safe.

The advantages and benefits of using microbial treatment in biodegrading long chain paraffins are:

1- There will not be any paraffin precipitation or deposition problems along production flow line.
2- The viscosity of crude oil will be reduced and there will be an increase in API.
3- The amount of paraffin will be reduced.
4- Decrease in pour and cloud points of the crude oil at the same time.

MATERIAL AND METHODS

Bacterial Isolation Technique

The first experiments were performed in the chemostat by preparing two liters of enrichment salts media in culture vessel and autoclaving at 121° C for 30 min. After sterilization the system was started up with temperature adjusted to 37° C, pH = 7.3 and agitator 250 rpm.

These experiments were repeated several times with different seawater sediment samples. After a laboratory screening program, the naturally occurring bacterial isolates from waste hydrocarbon polluted site, as pure culture or natural bacteria consortia, were selected as the best degraders of paraffinic oil and used in the rest of the experiments.

Six pure bacterial strains were isolated from sea water sediment and one additional species was isolated from Sarrir crude sample.

Most of the isolates were grown in mineral salts media and produced biosurfactants on waxy crude, n-hexadecane was used as a source of energy and carbon.

The biosurfactants production has been verified by the kerosene tests. The performances in degradation of hydrocarbon contained in paraffinic oils or in paraffin depositions, have been investigated in aerobic conditions on a rotary shaker (in Erlenmeyers flasks of 250 ml) at 37° C for 7-10 days.

For the determination of bacterial ability in the degrading of hydrocarbons containing paraffin depositions, the crude oil extraction methods were implemented (ASTM D 5369-13).

Experimental Culture Conditions

The bacteria were cultivated in a medium containing either 1%, 5%, 10% (vol/vol) of n-hexadecane and crude oil as a carbon and energy source plus 1.5 g/l $(NH_4)_2SO_4$, 4.465 g/l K_2HPO_4, 1.5 g/l $NaH_2PO_4.H_2O$, 0.2 g/l $MgSO_4.7H_2O$, 2 ml trace element solution per litre of medium. Cultures were cultivated in 250 ml Erlenmeyer flasks with 50 ml of medium and incubated with shaking (150 rpm) at 37° C.

Optical Density

The turbidity of the cultures was determined by measuring the optical density (O.D) at a wave length of 540 nm in 2 ml cuvettes using a spectrophotometer.

Biomass (dry weight)

The net dry weight for the dry biomass was determined. 1 ml of culture broth was centrifuged at 1500 rpm for 30 minute then washed with distilled water, vortexes and poured in certain container with a known weight then dried over night at 90° C to constant weight, and cooled for reweighing.

Relationship between the Optical Density and the Dry Weight Biomass

During the batch experiments, the optical density and the dry mass were determined simultaneously. The linear relation between OD_{540} and dry mass was obtained.

Biosurfactant Detection

To detect the presence of the biosurfactant the following tests must be conducted:

1. Xylene or oil emulsification assays.
2. Thin-layer chromatography (TLC)
3. Surface and interfacial tension measurements.

Emulsification Activity and Measurements

There are two procedures performed in this study to measure the emulsification activities as follows:

1. Culture broth was made cell free by centrifuging. 3.5 ml of the broth. Then it was vigorously shaken with 2 ml of toluene and xylene on a vortex shaker and left undisturbed. After one hour, optical density of the oil-in-water emulsion phase was measured at 610 nm wave length. The O.D. was reported as the emulsification activity. After 24 hours the height of the emulsion layer (water-in-oil) was measured and emulsification activity was expressed in cm. The test tubes utilized for activity measurements have diameters of 1 cm, capable of handling a 2 cm substrate layer, which corresponds to 2 mls of tested substrate (Banat, *et al* 1991).

2. Emulsification activities were also measured using the method of Cooper and Goldenberg. In this method; 2 ml of kerosene are added to 2 ml of the culture broth in a screw cap test tube and vortexes at high speed for 2 minutes using VORTEX TOP MIX. The emulsion stability was determined after 24 hours and the measured height of the emulsion layer was divided by the mixture total height and multiplied by 100 (Benbatla, 1995, Bicca, *et al*. 1999).

Gas Chromatographic Analysis

The gas chromatography was used in this research for the determination of the residual content, and the degree of biodegradation on crude oil effluents.

- **Residual Oil**

The residual oil was collected by extraction with a mixture of n- hexane and dichloromethane (1:1). All samples were collected and analyzed by G.C for n-alkanes before and after treatments.

- **Crude Oil Effluent Biodegradation**

The degree of biodegradation of the crude oil

effluents was determined using the chrompack model 439 capillary gas chromatograph equipped with a flame ionization detector (FID), a split / splitless injector and cp-sil 5 CB column (50 m, 0.32 mm, 0.12 μm film thickness). The gas chromatographic conditions were realized with a 300° C detector, 300° C injector, split ratio on 100:1, carrier gas helium flow rate of 62 Kpa and samples of 0.1μl injection. The column temperature of 40° C held 2 minutes, and then increased at a rate 5° C/min and final temperature 300° C for 30 minutes

Future Research Work

The laboratory pilot tests were designed as" flow equipment" simulating the alternation of stationary and flowing periods of the paraffinic crude oils during the production process.

At the end of tests on "flow equipment" samples of the circulated mixture will be collected and analyzed for fluid rheology, viscosity, pour point, wax content and API gravity. This research work investigates the following aspects:

1. The degradation of heavy fractions of crude oil into light fractions.
2. The reduction in viscosity and pour point tempeature of the crude oil.
3. The production of biosurfactents and organic acid to lower the surface tension and interfacial tension.

RESULTS AND DISCUSSIONS

The individual community members which were isolated from the local environment are found and considered to be Actinomycetes, Pseudomonas and Bacilli. This identification was achieved by direct analysis with epifluorescence microscopic observation. All genera display much variation in morphology and capsulation.

The specific growth rate and net dry weight of the different isolates were determined and illustrated in Figures 1 and 2. These figures indicate the effluence of the specific growth rate and biomass precipitation on a period of bacterial cultivation in mineral salts medium containing 0.5% (vol/vol) n-hexadecane. The highest specific growth rate was observed on PRCW B_1, PRCW E_1 with μ_{max} (0.243 h^{-1}) and (0.1926 h^{-1}) respectively. These bacterial isolates were selected for further investigations, since the PRCW B_1 and PRCW E_1 have optimum E_{24} and growth rate over the other isolates (Table 1).

The emulsification index results showed the ability of the isolates to grow with water immiscible hydrocarbon such as kerosene, toluene, xylene and crude oil. This indicates the production of surface-active compounds by the microbial culture, which has been shown to aid the metabolism of the substrate and stimulate microbial growth.

Table 2 shows emulsification index of six isolates on different source of hydrocarbon where all values

Table 1. Maximum growth rate of six isolates.

Bacterial ID	Growth rate (μ_{max}), hr-1
PRCW A_1	0.0673
PRCW A_2	0.1365
PRCW B_1	0.2430
PRCW E_1	0.1926
PRCW E_2	0.0562
PRCW B_2	0.0385

Table 2. Emulsification index of six isolates.

Emulsification index percent				
Bacterial ID	Toluene	Xylene	Crude	Kerosene
PRCW B_1	83	93	100	90
PRCW E_1	30	60	93	66
PRCW A_1	25	50	83	36
PRCW B_2	40	42	100	50
PRCW A_2	50	50	83	53
PRCW E_2	0	0	90	0

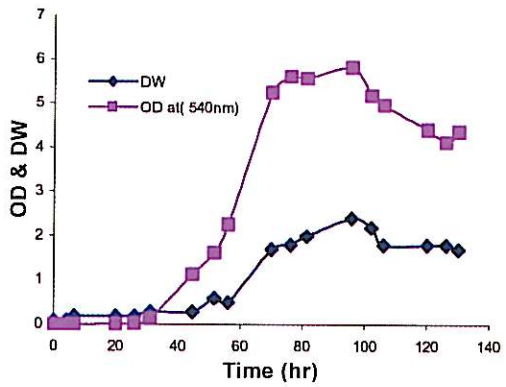


Fig. 1. Growth rate of bacteria type PRCW A_2 (OD = optical density; DW = dry weight (mg/ml)).

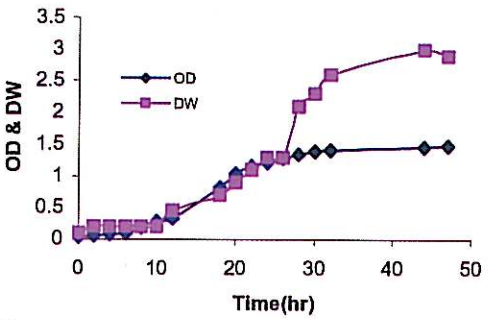


Fig. 2. Growth rate of bacteria type PRCW B_1 (OD = optical density; DW = dry weight (mg/ml)).

of emulsification index on crude oil are greater than values which was obtained on kerosene and other hydrocarbon source, these values reached to (E_{24}=100%) for PRC W B_1, PRC W B_2 and (E_{24}=93%) for PRCW E_1 at about 120 h, Figure 3 shows these results.

A measure of E_{24} on kerosene showed small quantity of surfactant was initially present in the culture broth. After approximately 48 hours of growth, the E_{24} value increases and reaches its maximum value at about 120 h (E_{24}=90%) for the isolate PRC W B_1. There is no any emulsification activity on PRCW E_2 {PRC W E_2 source isolation crude oil}.

Optical density and dry mass were determined simultaneously. The linear relation between OD_{540} and dry mass was obtained as shown in Figures 4 and 5.

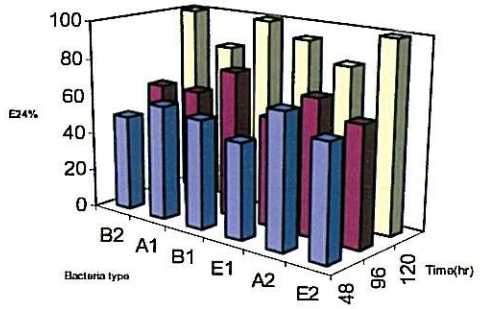


Fig. 3. Emulsification index on crude oil.

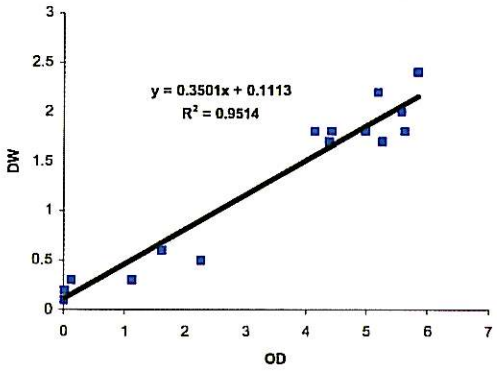


Fig. 4. Relation between biomass and optical density for bacteria PRCW A_2.

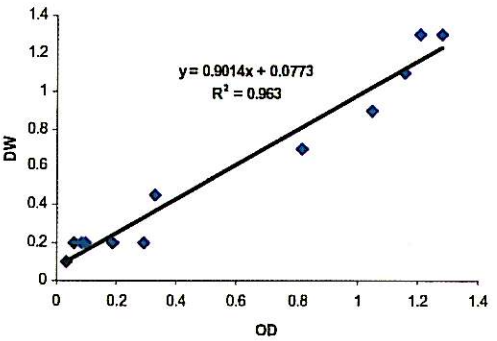


Fig. 5. Relation between biomass and optical density for bacteria PRCW.

Different isolates were able to produce a significant amount of biosurfactants as detected by water-in-oil and oil-in-water emulsions, during their growth on 1% of n-hexadecane. PRCW B_1 showed better performance (height of emulsion 4 cm) when grown for 120 hours in toluene and xylene. These bacterial isolates have good emulsification activities which appeared and were detected by absorbency, as showed in Figures 6 through 9.

The effects of hydrocarbon concentration on different isolates were studied in a batch culture system with different concentration 10 vol%, 5 vol%, 1 vol % of crude oil, Table 3 showed optimum growth rate at 1% with μ_{max} = 0.113hr^{-1} for PRCW E_1 and faster growth shown on PRCW

Table 3. Growth rate of six isolates on different concentrations of crude oil.

	Growth rate , hr^{-1}		
Bacterial ID	10%	5%	1%
PRCW A_1	0.028	0.0373	0.040
PRCW B_1	0.100	0.0852	0.093
PRCW B_2	0.027	0.0241	0.020
PRCW E_1	0.110	0.0500	0.113
PRCW E_2	0.027	0.0430	

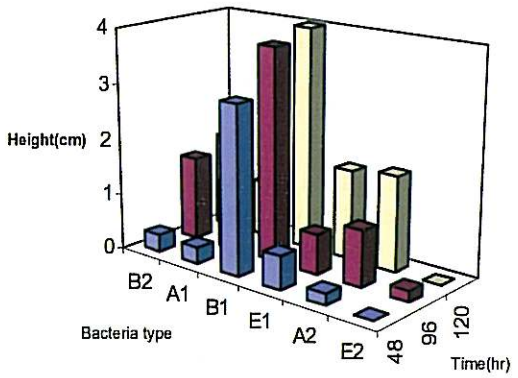


Fig. 6. Water-in-oil emulsification activities in the cell-free culture fluids of the bacterial strains grown and tested on toluene.

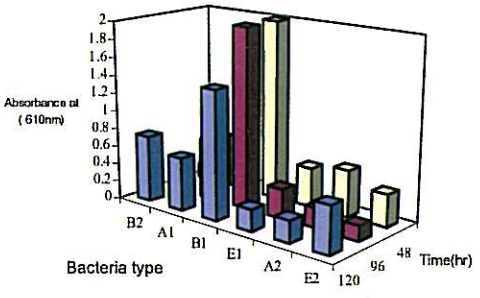


Fig. 7. Oil-in-water emulsification activities in the cell-free culture fluids of the bacterial strains grown and tested on xylene.

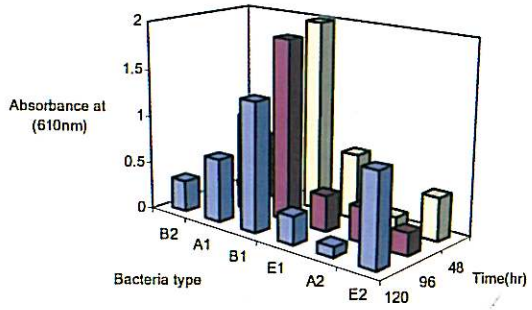


Fig. 8. Oil-in-water emulsification activities in the cell-free culture fluids of the bacterial strains grown and tested on toluene.

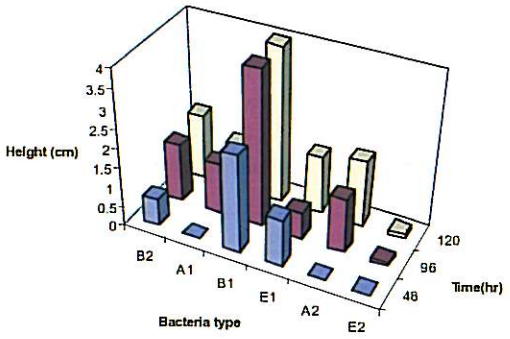


Fig. 9. Water-in-oil emulsification activities in the cell-free culture fluids of the bacterial strains grown and tested on xylene.

B_1, as explained in Figure (10). PRCW B_1 showed nearly the same growth on crude oil concentration 10% by volume, 1% by volume, with $\mu._{max} = 0.1hr^1$ and $\mu._{max} = 0.093hr^1$ respectively, PRCW A_1 showed best growth on 10 vol%, with $\mu._{max} = 0.04hr^{-1}$ and PRCW B_2 best growth on 1 vol%, with $\mu._{max} = 0.027hr^{-1}$.

The laboratory analysis was performed on treated and untreated crude oil samples using gas chromatography. The spectrums of GC analysis have been illustrated in Figures 11 through 13. The results showed a change in the distribution of alkanes and a decrease in the long chain carbon paraffins and an increase in the lighter fraction on isolates PRCW A_1, B_1, B_2 and E_1, while the other

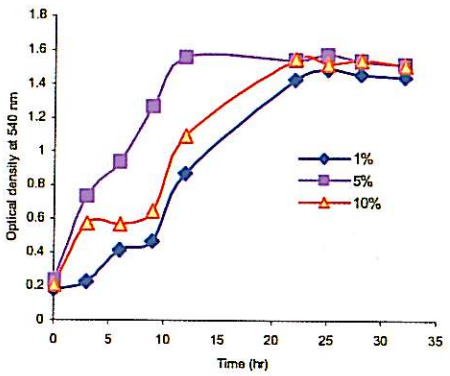


Fig. 10. Growth rate of bacteria PRCW B_1 on different concentrations of crude oil.

species did not show the same effect. Moreover, the concentration changes of n-alkanes obtained from GC analysis have been shown respectively in Figures 14 and 15.

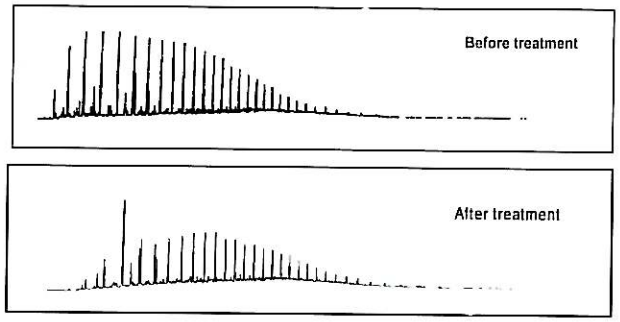


Fig. 11. Comparison of GC spectrums of crude oil before and after treatment with bacterial type PRCW A_1.

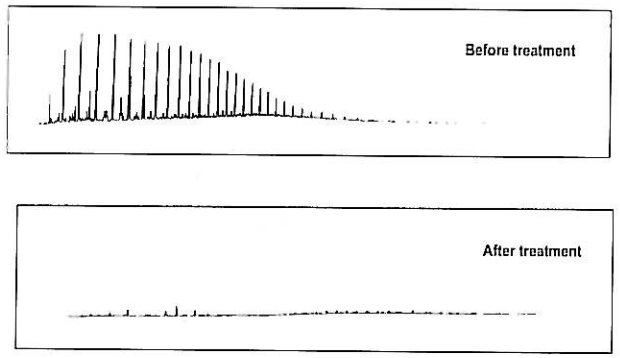


Fig. 12. Comparison of GC spectrums of crude oil before and after treatment with bacterial type PRCW B_1.

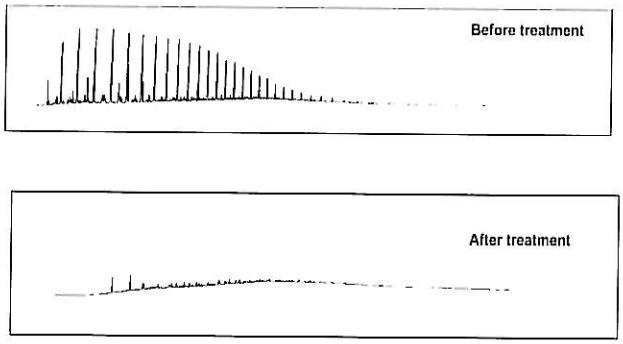


Fig. 13. Comparison of GC spectrums of crude oil before and after treatment with bacterial type PRCW E_1.

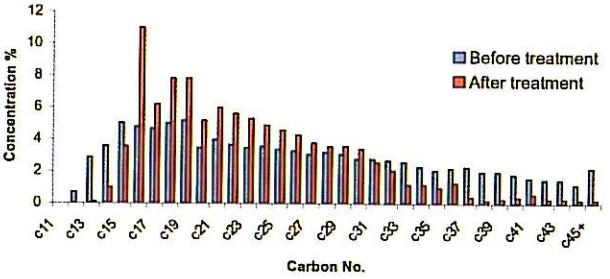


Fig. 14. GC. analysis of treated crude oil (5% concentration) with isolate PRCW A_1 after 21 days.

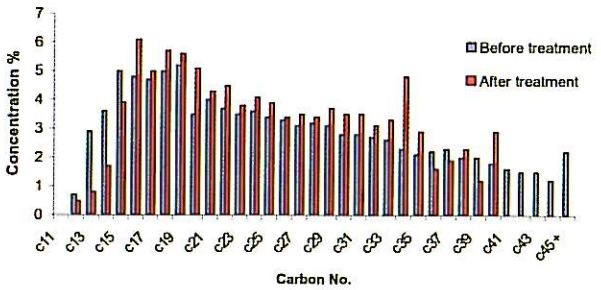


Fig. 15. GC. analysis of treated crude oil (5% concentration) with isolate PRCW B_2 after 21 days.

CONCLOUSIONS

1. Several different bacterial hydrocarbon degraders were detected in pure consortium from sea water sediment contaminated by waxy crude oil.

2. Specific bacterial cells PRCW B_1 have shown emulsification activity up to 100%, while the other species such as PRCW E_1 shows 93% emulsification activity. These two isolates can be targeted for selection in preventing or controlling wax deposition in field application.

3. After microbial treatment degradation rate by PRCW B_1 isolates on Sarir crude samples showing the highest values of n-alkanes reduction when exposed to PRCW B_1.

4. The same growth rate was achieved with PRCW B_1 in the concentration of 1% and 10% of crude oil which means that this type of isolates could be used in the field trial to prevent and control wax deposition.

5. PRCW A_1, B_1, B_2 and E_1 isolates have shown greater reduction rate of the heavy fraction of the original waxy crude oil sample (Sarir crude) due to their higher emulsification performance.

RECOMMENDATIONS

1. Biodegradation of bacteria for higher concentration of crude oil has to be verified specifically for 30% or higher.

2. Perform rheology tests for examining the isolates to determine the API gravity, cloud, pour point temperatures and viscosity.

3. Dynamic flow test experiments need to be carried out for simulating the field conditions.

REFERENCES

American Standard Test Method. ASTM D 5369-13.

Banat. M., Samarh. N., Murad. M., Horne. R. and Banerjee. S. 1991. Biosurfactent production and use in oil tank clean-up. Wld J. Microbiol. Biotechnol. 7,80-88.

Banat, I.M., Makkar. R.S., Cameortra S.S. 1999. Potential commercial applications of microbial surfactants. Appl. Microbiol. Biotechnol .53, 495-508.

Benbatla, S. 1995. Isolation of biosurfactent producing bacteria from oil contaminated soils. November Boumerdes 35000 Alger, 289-294.

Bicca. F. C., Fleck L.C., M.A. and Zachia. 1999. Production of biosurfactant by hydrocarbon degrading *Rhodococcus* rubber and *Rhodococcus erythropolis*. Rev.microbiol.30, 0001-3714.

Cooper, D.G. 1982. Biosurfactents and Enhanced Oil Recovery, pro.int. Conf microbial enhanced oil recovery, Afton, ok, doe conf-85051 .40, 112-114.

Rocky Mountain Oil Field Testing Center. December 17, 1997. Chemical and microbial paraffin control project.

Lazar, I., Voicu, A., Nicolescu, C., Mucenica, D., Dobrota, S., Petrisor, G. I., Stefanescu, M. and Sandulescu, L., 1999. The use of naturally occurring selectively isolated bacteria for inhibiting paraffin deposition, Journal of Petroleum Science and Engineering. 22, 161-169.

Sadeghazad, A. and Ghaemi, N., 2003. Microbial prevention of wax precipitation in crude oil by biodegradation mechanism. Society of petroleum engineers. SPE 80529, 1-11

Technical memorandum B-1.July 10, 2002. Microbial technology for improvement of oil quality.

Petroleum Res. J. Vol. 17 (2005); P. 67–72, 11 Figs.

Evaluation of Imidazoline-based Inhibitors for Oil Environment by Means of Advanced Eelectrochemical Methods

G. Gusmano*, G. Montesperelli**, P. Labella***, A. Privitera*** and S. Tassinari***

تقييم مثبط التآكل المكون من مادة إميدازولين لإستخدامه في البيئة النفطية بإستخدام أساليب كهروكيميائية متقدمة

ج. قوسمانو وج. مونتيسبيريلي وب. لابيلا وأ. بريفيتيرا وس. تاسيناري

تتطرق هذه الورقة الي النتائج الأولية لإختبارات تقييم نشاط مثبطات التآكل المكونة من مادة إميدازولين بإستخدام طيف المعاوقة الكهروكيميائية بالإضافة الي طرق كهروكيميائية تقليدية أخرى.

أجريت الإختبارات على عينات من الفولاذ الطري نوع AISI 1040 مغمورة في محلول يحاكي تركيب الطور المائي المصاحب للزيت الخام أثناء عمليات إنتاج ونقل النفط أي أنه شديد الملوحة ويحتوي علي غاز ثاني أكسيد الكربون ويوجد في بيئة لاتحتوي على الاوكسجين وعند درجة حرارة 40 درجة مئوية.

تم إختبار تركيبتين مختلفتين للمثبط. حللت معطيات طيف المعاوقة الكهروكيميائية بواسطة الدوائر المكافئة وقد مكنت الإختبارات الكهروكيميائية التقليدية من إثبات آليات وأنماط نشاط مختلفة وذلك حسب المثبط.

Abstract: *In this paper preliminary results of tests for the evaluation of the activity of imidazoline-based corrosion inhibitors by means of Electrochemical Impedance Spectroscopy (EIS) and other traditional electrochemical methods are reported. Tests have been carried out on AISI 1040 mild steel specimens immersed in solution simulating the composition of aqueous phase during oil production and transportation: high salinity, presence of CO_2, anaerobic environment, temperature 40 °C. Two different inhibitor formulations were tested.*

EIS data have been analysed by means of equivalent circuits. The electrochemical tests permitted to evidence different mechanisms and activity depending on inhibitor formulation.

* Dipartimento di Scienze e Tecnologie Chimiche, Universita di Roma "Tor Vergata".

** Dipartimento di Fisica ed Ingegneria dei Materiali e del Territorio Universita Politecnic Marche.

*** Ondeo-Nalco Italia s.r.l.

INTRODUCTION

The environmental conditions in oil fields can be very different but they could be assumed follow: anaerobic conditions, high concentration of CO_2 (often close to saturation), high salinity, variable concentration of sulphide ions[1-2] and high temperature.

Depending on composition, different forms of corrosion can take place in oil and gas wells and flow lines[3]. Amongst them, CO_2 corrosion, usually called sweet corrosion, is one of the most severe.

The main method of protection all petrochemical facilities in the world is the use of inhibitors, because of their great flexibility by adjusting their concentration in relation to environmental corrosivity.

The most effective corrosion inhibitors for oil and gas pipeline application are the fatty acid imidazoline. About 90% of inhibitor used by oil companies is based on the use of aliphatic long chain diamines or imidazolines. The action mechanism of imidazolines, whose general structure is depicted in Figure 1, is not well understood[4-8]. It has been reported that

imidazolines form a double layer on the metal surface and that their activity depends on the nature of the hydrocarbon tail, but many details have to be cleared, in particular regarding their action mechanism.

In this paper some results of a research program on the evaluation of two different imidazoline-based inhibitors are reported. In particular, tests on carbon steel specimen have been carried out by means of different electrochemical methods such as: Open Circuit Potential (OCP), Polarization Curves (PC), Linear Polarization Resistance (LPR) and Electrochemical Impedance Spectroscopy (EIS).

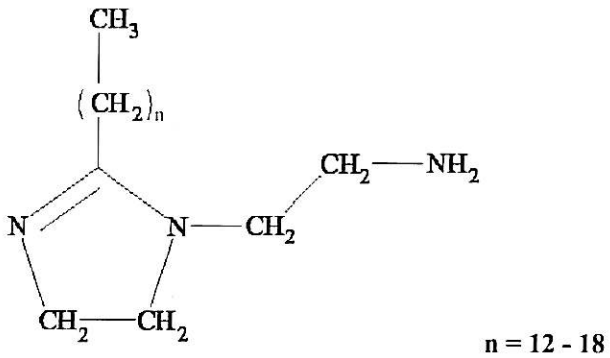


Fig. 1. General chemical structure of imidazolines used in this work.

EXPERIMENTAL

Tests have been performed on AISI 1040 cylindrical electrodes, 4 mm in diameter. Surface electrode was delimitated by enamel and the immersed area was 10.2 cm^2.

Tests were carried out in an unstirred solution of 30 g/l sodium chloride in which a constant CO_2 bubbling was performed throughout tests. A sealed cell was used with a vent to prevent over pressure. The cell was thermostat-controlled at 40° C and oxygen concentration was measured by an Orbisphere Laboratories Model 2713 probe, and kept below 10 ppb during all the tests.

Inhibitors were a commercial mixture of imidazolines with an aliphatic chain varying between 12 and 18 carbon atoms, as shown in Figure 1. Two different inhibitors formulation, supplied by Ondeo-Nalco, at concentration of 25 or 50 ppm were used and their compositions are reported in Table 1. Inhibitor A contained acetic acid as salting agent whereas inhibitor B contain a mixture of acetic acid and thioglycolic acid. Blank tests were also performed.

EIS measurements were carried out at the OCP in the frequency range $5x10^{-3}$ -$5x10^{5}$ Hz with an A.C. signal of 5 mV by a Solartron 1260 Frequency Response Analyser (FRA) and a 273 E.G. & G. Princeton Applied Research Potentiostat-Galvanostat. Equivalent circuit evaluation of EIS data was performed by Z-Plot software (Scribner Ass.) using a Non Linear Least Squares (NLLS) algorithm.

Corrosion rate measurements were performed by Linear Polarization Resistance (LPR) method by an ADSE corrosimeter using a three-electrode corrosion probe.

Polarization Curves were performed with a scan rate of 4 mV/s.

Table 1. Composition of inhibitors (% Wt)

Components	Inhibitor A	Inhibitor B
Imidazolines	25	25
Acetic acid	6	3
Thioglycolic acid	-	3
Isopropanol	10	10
Water	balance	balance

RESULTS AND DISCUSSION

The OCP trend of specimens in inhibited solution (50 ppm) is shown in Figure 2, in which, as a comparison, the OCP for a blank test is also reported. OCP curves of tests in inhibited solution showed a clear ennoblement from the first hour of immersion. No relevant differences were detected between inhibitors A and B. After 4 hours, OCP kept a constant value in the range between -650 and -640 mV (Vs AgCl) for inhibited tests, while the blank test settled at about -710 mV.

Polarization curves were performed at the same condition. Figure 3 reports polarization curves of tests with inhibitor A at 50 ppm, immediately after the immersion and after 2 and 6 hours. Polarization

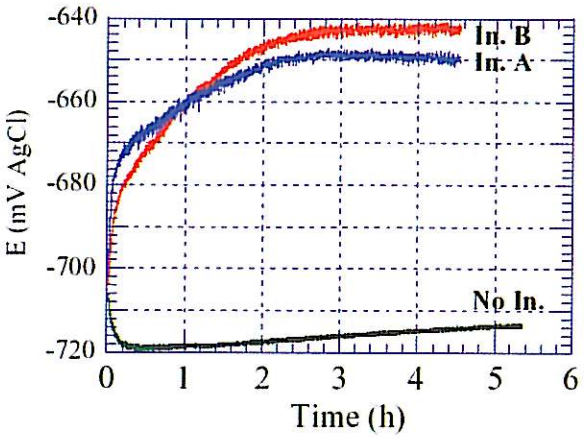


Fig. 2. OCP as a function of immersiontime (Inhibitor concentration: 50 ppm).

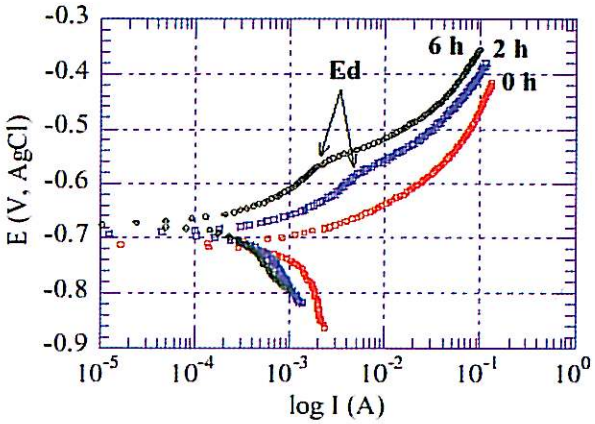


Fig. 3. Polarization curves for inhibitorA at 50 ppm, at different immersion time.

curves show an OCP shift towards anodic direction and the concurrent increase of both anodic ($\bullet_a$) and cathodic ($\bullet_c$) Tafel slopes with time, typical of adsorption inhibitors. Within the anodic part of curves collected after 2 and 6 hours of immersion, a slope variation can be detected, indicated by the arrow in Figure 3. This behaviour reveals the potential at which the film breakdown takes place and it is usually called desorption potential (E_d)[9].

A slight increase of E_d with time can be detected (from –584 to -557 mV). Data of polarization curves taken after 6 hours for both the inhibitors are summarised in Table 2.

Table 2. – $\bullet_a$, $\bullet_c$ and E_d after 6 hours

Blank Inhibitor A	Inhibitor B
•a (mV) •c (mV) Ed (mV)	93 130 129 318 217 89 - - 557 -439

Inhibitor B shows an increase of E_d, stronger than that observed for inhibitor A, thus indicating a higher film stability with respect to inhibitor A.

The results of LPR measurements, shown in Figure 4, demonstrate that corrosion rate for inhibitor

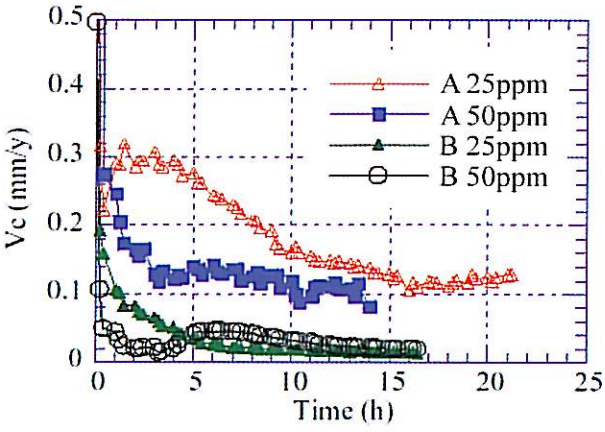


Fig. 4. Corrosion rates by LPR.

A at 25ppm settled at 0.15 mm/y after about 12 h of immersion, while for the same inhibitor at a concentration of 50 ppm reached a corrosion rate of 0.10 mm/y in a shorter time. The same measurements for inhibitor B showed corrosion rates lower than 0.02 mm/y after only 5 hours for both concentrations. LPR tests for blank tests gave an average corrosion rate of 1.40 mm/y.

EIS measurements were performed in three different conditions: without inhibitor and in the presence of inhibitors A and B at the concentrations of 25 and 50 ppm.

The analysis of EIS data, acquired during blank tests, shows that this system is described by a simple RC parallel equivalent circuit, as reported in Figure 5a, being R_s the electrolyte resistance, R_{ct} the charge transfer resistance and CPE_{dl} the double layer capacitance. No circuit element that can be related to the presence of any protecting film on metal surface was detected. No contribution from diffusion (Warburg impedance) was also detected, since the oxygen concentration within the cell was negligible. The equivalent circuit has been developed using Constant Phase Element (CPE) instead of real capacitance because of the semiarc depression in the Nyquist plot. The contribution of CPE to total impedance is given by $½ = Y_o (j\omega)^n$ in which Y_o is the admittance and n a parameter associated to the semiarc depression with respect to real axis. If n = 1, CPE contributes as an ideal capacitance.

R_{ct} values for blank test varied in the range between 10 and 20 Ohm, thus confirming the high corrosion rate V_c measured by LPR. C_{dl} was high, in the range 4-6 mF, due to the presence of a high charge concentration on electrode surface.

EIS spectra acquired in inhibitor A solution were described by the equivalent circuit of Figure 5b, in which two additional elements are present: the film resistance (Rf) and capacitance (CPE_f). This is a

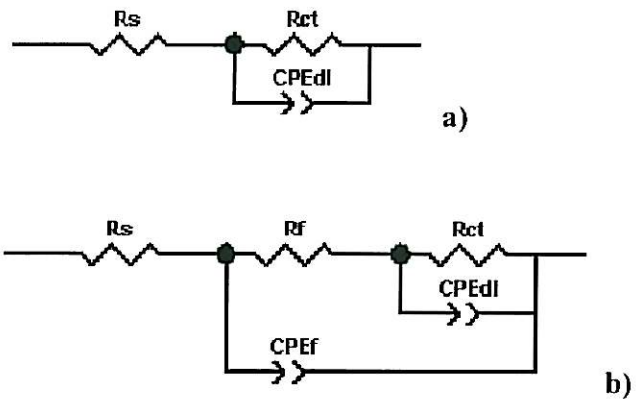


Fig. 5. Some of the equivalent circuits used in this paper.

generally accepted equivalent circuit to describe the corrosion behaviour of film-coated metals, where the metallic substrate is exposed to the electrolyte through the permeable defects (*e.g.* pores) present in the film[4-10].

The use of this equivalent circuit permitted a good simulation of the EIS data as shown in Figure 6 for a spectrum related to a test with inhibitor A at 50 ppm. The f^2 test and Weighted Sum of Squares (WSoS) values were respectively 4.2 10^{-4} and 3.6 10^{-2} for circuit 5b, thus confirming good fitting.

The use of equivalent circuits with NLLS-fit (an extension of least squares regression method) permitted to calculate the charge transfer and film parameters during test. According f^2 test (the square of the standard deviation between the original data and the calculated spectrum) and WSoS values, the error associated to circuit element estimation was always < 5 %. The first EIS spectra acquired few minutes after the immersion indicated only one semiarc that, on the basis of capacitance values, can be ascribed to charge transfer reaction. With increasing of immersion time, charge transfer characteristic moved towards low frequency and a strong increasing in total resistance was observed. After few hours of immersion, a second time constant was observed in the high frequency region (indicated by the arrow in Figure 6). This new time constant can be attribute to the imidazoline film formation. Figure 7 reports R_{ct} and R_f trend for a typical test in inhibitor A at 50 ppm.

R_{ct} and R_f have very similar trends characterized by a marked increase in the first part of the test, confirming that the film formation is fast. After 10 hours, R_{ct} settled at a constant value of about 1350 Ohm whereas the trend of R_f was still increasing.

Figure 8 reports, the trend of C_{dl} and C_f for the same test as Figure 7. C_{dl} and C_f show an inverse trend, with strong decrease for C_{dl} in the very first part of the test and a slight increase for C_f during the first 20 hours of the test. After that, both capacitances become constant and very close to a value of about 870 ^F.

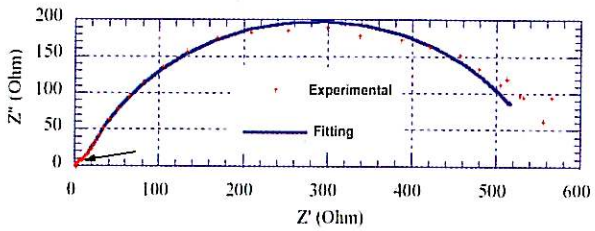


Fig. 6. Fitting of a typical Nyquist plot for a test with inhibitor A, using the equivalent circuit in figure 5b.

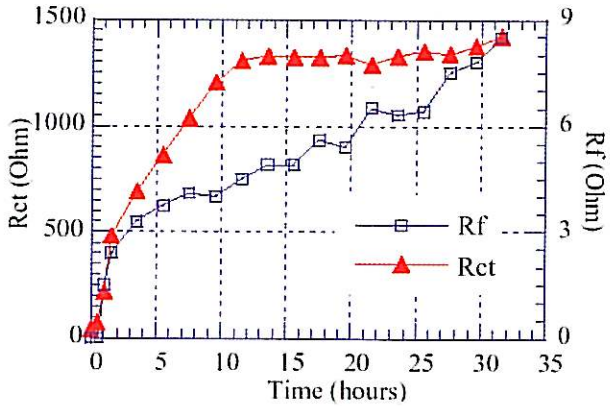


Fig. 7. R_{ct} and Rf trend as a function of time for a test in inhibitor A at 50 ppm.

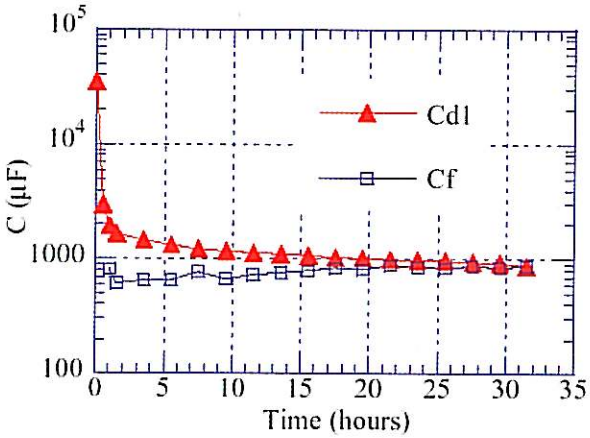


Fig. 8. C_{dl} and C_f trend as a function of time for a test in inhibitor A at 50 ppm.

EIS spectra, acquired on tests with inhibitor B, showed a more complex outline. Circuit in Figure 5b did not allowed to have good fit, thus suggesting a more complex film-metal interface structure with respect to inhibitor A. For this reason, the analysis of EIS data on inhibitor B required the addition of a new RC circuit as shown in Figure 9. This new RC circuit, whose parameters have been labeled R_z and C_z, can be ascribed to the effect of thioglycolic acid to film build up.

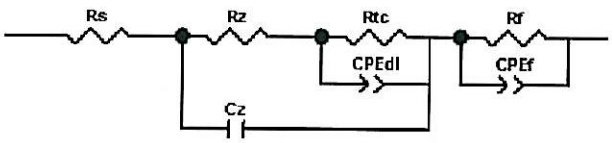


Fig. 9. Equivalent circuit used to fit EIS spectra on inhibitor B.

Resistance values as a function of immersion time are shown in Figure 10. R_{ct} and R_f have the same trend since both of them are related at the film formation. R_f is about one order of magnitude higher with respect to that of inhibitor A. As a consequence of this, R_{ct} reached a steady value of 3500. R_z gave a poor contribution to the total resistance (about 15•)

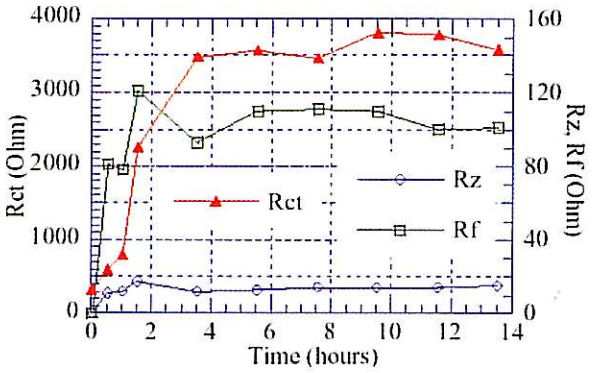


Fig. 10. R_{ct}, R_f and R_z as a function of time for a test in inhibitor B at 50 ppm.

and is essentially independent on time. As a first assumption, thioglycolic acid seems to be inaccessible by solution, acting as an inner layer and the very low R_z suggesting that it is not protective itself. It is well known that thioglycolic acid decompose in the presence of heavy metal to produce hydrogen sulfide and an FeS precipitation could be hypothesized.

C_{dl} has a trend very similar to that of inhibitor A: after a slight decrease, reached a constant value of 500 ^F. On the other hand, C_f decreases during first hours of immersion, probably because of the increasing of film thickness since the capacitance is inversely proportional to it.

C_z contribution is small and approximately unaffected by immersion time as well as R_f. It can be assumed that its effect takes place in the very first part of the film build up (Fig. 11).

As a general remark, EIS data suggest that the presence of thioglyc olic acid or of sulphides, coming from its decomposition, can influence the kinetic of imidazoline adsorption on metal surface, thus resulting in an improvement of activity. The role played by thioglycolic acid is not clear. It could adsorb or chemisorb on metal surface, by means of mercapto

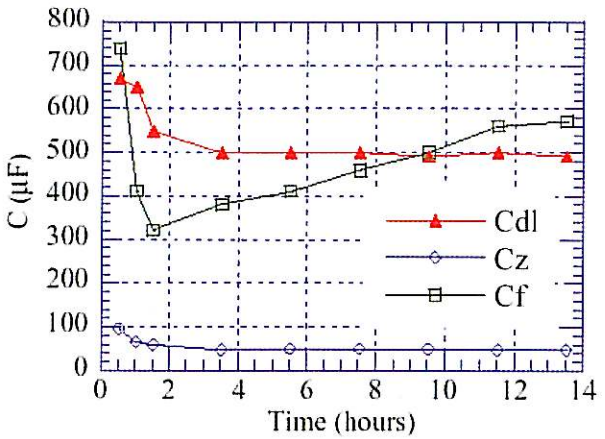


Fig. 11. C_dl, C_f and C_z as a function oftime for a test in inhibitor B at 50 ppm.

(HS$^-$) group or decompose to form FeS that can form an inner layer on which imidazoline can bond heavily. Surface analysis such as FTIR and XPS will be performed to clarify this point.

CONCLUSION

The present paper reports results of the evaluation of the activity of two formulations of imidazoline-based inhibitors for oil field environment.

Data have shown a positive effect of thioglycolic acid on inhibition mechanism. Polarization curves indicated the formation of a protective film, whose desorption potential increase with immersion time and moving from inhibitor A to B. The use of inhibitors permitted reduction of corrosion rates from 1.40 to 0.02 mm/y.

EIS data have been evaluated by three equivalent circuits that permitted the determination of film and charge transfer contribution to total resistance. Two different action mechanisms were detected.

REFERENCES

[1] El Hosary, A. A., *et al.*, 1995. 8 SEIC; Univ. Ferrara, p. 1269.

[2] Choi, H. J., Cepulis R. L., Lee, J. B., 1989. Corrosion, **45**, 943.

[3] *Metals Handbook* ninth edition, 13., p. 1232, ASM International, Metals Park,Ohio.

[4] Tan, Y.J., Bailey S. and Kinsella, B.; 1996. *Corrosion Science* **38**, 1545-1561.

[5] X. Zhang X., Wang F., Y. Du Y. He, Y.; 2001. *Corrosion Science*, **43**, 1417-1431.

[6] Wang D. Ying S. Li Y. *et al.*, 1999.*Corrosion Science* **41**, 1911.

[7] Szyprowski A.J., proceedings of 8 SEIC; 1995. Univ. Ferrara p. 1229.

[8] Edwards A., Osborne C., Webster S. *et al.*; 1993. *Corrosion Science*, **36**, 315.

[9] Wang J., C. Chin Cao, J. 1996. *Soc. Corrosion Protect*, **1**, 69.

[10] Lorenz W.J., Mansfeld F., 1981. *Corrosion Science* **21**, 647.

Petroleum Res. J. Vol. 17 (2005); P. 73–80, 10 Figs.

Integrated Methodology for Mineral Scale Inhibitor Squeeze Treatments

B. Bazin, N. Kohler and A. Zaitoun*

طريقة متكاملة لمعالجة تكوّن قشور معدنية بضخ مواد كيميائية

ب. بازين ون. كوهلر وأ. زيتون

إن ترسب القشور المعدنية لا يقتصر في العادة على المعدات السطحية وأنابيب البئر، ولكنه يتعداها ليشمل المنطقة القريبة من المكمن، ويأتي تكوّن قشور من الكبريتات نتيجة عدم توافق بين مياه الحقن البحرية وبين الماء المصاحب للتكوين الصخري، وتحدث الرواسب القشرية من الكربونات نتيجة لتعرض السوائل المنتجة لاختلافات مفاجئة في الضغط ودرجة الحرارة بين المكمن وعند السطح وما يصاحب ذلك من هروب مفاجئ لغاز ثاني أكسيد الكربون. وقد يخلق ترسب هذه المعادن نقصا في النفاذية نتيجة لانسداد الفتحات وهو ما يسبب تبعا لذلك نقصا كبيرا في إنتاجية البئر. وفي أغلب الأحيان لا يمكن تفادي تكوّن الرواسب القشرية، ولكنه دائما ما ينصح بالمعالجات الوقائية. ومن أهم التقنيات الفعالة التي تمنع ترسب قشور المعدن هو ضخ التكوين بنوع معين من مانع التآكل الكيميائي.

تقدم هذه الورقة طريقة متكاملة يتم استخدامها من قبل المعهد الفرنسي للبترول من أجل تعريف أفضل صياغة لمانع التآكل الكيميائي لنوع معين من العلاج بالضخ ولزيادة قدرة أدائها في المكمن الموازي. وتستعمل كل من الطريقة المعملية والعددية لاختيار موانع التآكل ولتقييم أدائها بمقادير سائبة تحت ظروف لب البئر والتعرف على أفضل استراتيجية لطريقة الضخ. وتحوي الاختبارات الكيميائية طرق الاختيار التقليدية التي تعتمد اختبارات ساكنة ومتحركة مختلفة بهدف تحديد أقل تركيز من مانع التآكل الكيميائي الذي يمكن بواسطته كبح تكون الرواسب القشرية، ويتم اضافة إلى مقارنة خواص موانع التآكل المستخدمة حاليا كالفوسفونات والمنتجات الجديدة صديقة البيئة على سبيل المثال، إجراء تجارب غمر البئر لتقييم خواص امتزاز ومجّ مانع التآكل تحت ظروف المكمن ومخاطر ضعف الإنتاج، وتمت عن النهاية المحاكاة العددية للعلاج باستعمال محاكاة مكمن محدد بهدف زيادة عمر المعالجة الكيميائية من مستوى المعمل إلى منزلة المكمن.

Abstract: *Mineral scale deposition often occurs not only in surface facilities and well tubing but also in the near well bore reservoir area. Sulphate scale formation is usually the result of poor compatibility between injected seawater and formation brine. Carbonate scales are mainly generated by abrupt pressure and temperature variations to which production fluids are submitted between reservoir and surface and the simultaneous loss of CO_2. The precipitation of both mineral deposits may create significant permeability impairments due to plugging of pore throats and consequently induce large well productivity loss. In most cases, scale formation cannot be avoided and preventive treatments are recommended. One of the most efficient techniques to prevent mineral scale deposition is the squeeze into the formation of a specific scale inhibitor.*

This paper presents an integrated methodology applied by IFP in order to define the best chemical inhibitor formulation for a specific squeeze treatment and to optimize its implementation into the corresponding reservoir. Both experimental

* Petroleum Research Centre, P.O. Box 6431, Tripoli, Libya.

and numerical approaches are used to select the inhibitors, to evaluate their performance in bulk and in core conditions, and to define the best strategy for the squeeze process. Laboratory tests include classical inhibitor selection methods based on static Jar Tests and dynamic Tube Blocking Tests in order to determine the Minimum Inhibitor Concentration (MIC) to prevent scale formation. The properties of current scale inhibitors, i.e. phosphonates, as well as those of new environmentally friendly products are compared. Core flooding experiments are performed to evaluate inhibitor adsorption / desorption properties at reservoir conditions and the risks of production impairments. Numerical simulations of the treatment are finally performed using a specific reservoir simulator to upscale the squeeze life time of the treatment from the laboratory to the reservoir level.

INTRODUCTION

Scale inhibitor squeeze treatments provide one of the most common and efficient methods to prevent the formation of mineral scales in producing wells. Scaling is an undesirable precipitation caused by either mixing of incompatible waters or rapid changes of the thermodynamic conditions during fluid production. The nucleation and growth of salt crystals can occur both in the production system or in the near wellbore formation. One of the most valuable techniques to prevent or to fight the scale formation is to inject, *i.e.* squeeze, a scale inhibitor directly into the formation.

A typical squeeze treatment consists of injecting a slug of the chemical formulation into the reservoir followed by the shut-in of the well. During the shut-in period, the inhibitor is retained into the formation. When production is resumed, the inhibitor is released back into the produced water and prevents scale formation. The success of the treatment depends on how long the inhibitor concentration in the flowing water is efficient to prevent scale precipitation. This concentration has, in fact, to exceed the Minimum Inhibitor Concentration (MIC).

The focus of this paper is to review the methodology which contributes to a successful squeeze treatment, starting with the scale identification, followed by a laboratory study in reservoir conditions for the selection of the best inhibitor to prevent scale formation and ending with the design of the well treatment. Laboratory tests include the classical inhibitor selection methods based on Jar Tests and Tube Blocking tests. The purpose of these tests is to select the inhibitor on the basis of its MIC in the critical formation water/injection water mixture. Core floods are then carried out in order to obtain the inhibitor dynamic adsorption isotherms. Numerical simulations of the treatment are performed using a specific reservoir simulator to design the squeeze life time of the treatment, based on laboratory determinations of the inhibitor MIC and adsorption values. This integrated methodology extending from the laboratory testing to the treatment design is illustrated on a case study where the scale consists essentially of calcium carbonate deposition at the producing well.

The paper is organized as follows. The first section is a presentation of the scaling problem. The second part describes the different experimental methods used for the MIC determination and the core flood tests. In the third section, we focus on the numerical simulations for the design of the treatment.

PRESENTATION OF THE SCALING PROBLEM

In the case study presented here, scaling is due to the change in the thermodynamic conditions when well fluids are produced, the actual formation water being unstable in surface conditions. A particular procedure must then be applied to prepare the critical formation water/injection water mixture. We reconstruct this water by mixing two simplified waters containing respectively twice the precipitating cation concentration or the precipitating anion concentration. The 50/50 mixture of both cation-rich and anion-rich waters will then have the same composition as the produced water (Tables 1 and 2).

The identification of the precipitating salts is performed with the PHREEQ[1] software. Two types of calculations are performed:

Table 1. Reconstruction of both cation-rich and anion-rich waters.

Salt	Cation-rich Water (ppm)	Anion-rich water (ppm)
$CaCl_2.2\ H_2O$	59 134	0
$MgCl_2.6H_2O$	17 131	0
KCl	1 484	1 484
NaCl	70 000	70 000
$NaHCO_3$	0	3 162
Final pH (25°C)	6.83	8.6

Table 2. Ionic compositions of the different waters (ppm).

Salt	Cation-rich water (ppm)	Anion-rich water (ppm)	50/50 mixture
Na^+	27251	28387	27954
K^+	777	777	777
Mg^{2+}	2048	0	1024
Ca^{2+}	16090	0	8045
Cl^-	77037	42620	59828
HCO_3^-	0	2296	1148
TDS	123473	74080	98776

- Evaluation of the risk of precipitation for the 50/50 mixture of cation-rich/anion-rich waters at the reservoir temperature and saturated with CO_2;
- Evaluation of the risk of precipitation for the same 50/50 water mixture but at the atmospheric CO_2.

The saturation index is defined as:

$$SI = \log IP/SP$$

where, IP is the ionic product, *i.e.* the product of the anion and cation concentrations, and SP is the thermodynamic solubility product at the desired temperature. If SI is positive the salt is likely to precipitate, if SI is negative or nil, the mineral is soluble and the solution is expected to be stable.

The results of the computer calculations are given in Table 3. Carbonate salts (aragonite, calcite and dolomite) are likely to form during formation water degassing in the well.

Table 3. Calculated saturation indexes at 65°C.

Salt	Cation-rich water (ppm)	Anion-rich water (ppm)	50/50 mixture
Na^+	27251	28387	27954
K^+	777	777	777
Mg^{2+}	2048	0	1024
Ca^{2+}	16090	0	8045
Cl^-	77037	42620	59828
HCO_3^-	0	2296	1148
TDS	123473	74080	98776

EXPERIMENTAL STUDIES

Laboratory work consists mainly of the determination of MIC by both Jar Tests and dynamic Tube-Blocking Tests (TBT) and of the adsorption/desorption of the tested inhibitor during core flood experiments. Several products are usually comparatively evaluated. Results presented below in some detail will concern principally a commercial organo-phosphonate, but data obtained with other potential inhibitors such as another phosphonate, a polyacrylate and representatives of two families of new inhibitors[2] claimed as being environmentally friendly, are also given for comparison purposes (Table 4).

Determination of the MIC

The Minimum Inhibitor Concentration (MIC) is determined by two different methods: the static Jar Test or Becher Tests and the dynamic Tube Blocking Test (TBT).

The Jar Tests are conducted following the NACE[3] Standard Test Method 0374-20013. According to this Test Method cation-rich and anion-rich waters are prepared with the inhibitor incorporated in the anion-rich water at twice its testing concentration. Final 50/50 water mixtures are stored in an oven at reservoir temperature and saturated with CO_2. They contain 0, 5, 10 and 15 ppm active matter of the inhibitor. For the commercial organic phosphonate no precipitation is observed for the 3 inhibitor concentrations, meaning that even a 5 ppm concentration of this inhibitor is sufficient for preventing the scale formation. Thus MIC for this inhibitor is less than 5 ppm in the 50/50 water mixture at reservoir temperature.

For the TBT measurements, the 50/50 water mixture is injected at constant flow rate (3 ml/min) by using two pumps, (one for the anion-rich water, the other one for the cation-rich brine) into an 8 meter long stainless steel capillary tube (internal diameter 0.5 mm) (Fig. 1). The pressure drop across the capillary is continuously measured as a function of time since the start of injection. A blank test is first run with the 50/50 water mixture. Then, the inhibitor is dissolved in the anion-rich brine at twice the desired testing concentration. The results show that for the blank test, the capillary is blocked in ~ 25 minutes. In presence of the commercial organo-phosphonate, the blocking time increases above the blank time with increasing inhibitor concentration (Fig. 2). A long term inhibition in tube blocking is observed for less than 5 ppm of this inhibitor. A concentration of about 2.5 ppm (active matter) is taken as the MIC for the inhibitor in these testing conditions (about 5 times the blank time is reached before blocking). It is concluded that a very good agreement exists in the determination of the MIC value by either the Jar Test or the Tube Blocking Test.

The inhibitors of Table 4 were comparatively tested in the same experimental conditions. Figure 3

Table 4. Experimentally tested inhibitors.

Commercial name	Chemical formula	Tested formulation L, S	Tested formulation AM %	Characteristics M_n	Characteristics M_w	Characteristics IP
Phosphonate (HEDP) Dequest 2010	1-Hydroxyethylidene (1-1 diphosphonic acid): HEDP	L	60		206	
Polyacrylate (PAA) Romax 7200	Carboxylate copolymer	L	53	2000	3000	1.5
Green Products Baypure DS 100 (PASP)	Polyaspartate	L/S	40/90	1740	4810	2.8
MS 10 ter (lab IFP)	Polyaspartate	S	90	3200	7400	2.3
Dequest PB (CMPS)	Carboxymethylated Polysaccharides					
	CMPS 14625 SD : 2.5 PD: 10	L/S	20/90	1730	5300	3
	SD : 2.5 PD : 24	S	90	4900	7300	1.5
	CMPS 14620 SD : 2.0 PD : 10	L/S	20/90	2160	6130	2.8
	SD : 2.0 PD : 24	S	90	3400	6000	1.8
	CMPS 14615 SD : 1.5 PD : 10	L/S	20/90	1760	4810	2.7

L = Liquid; S = Solid; AM = Active matter (weight %); SD= Substitution degree; PD = Polymerization degree; M_n = Average molecular weight (Size exclusion chromatography); M_w = Average molecular weight (Light scattering).

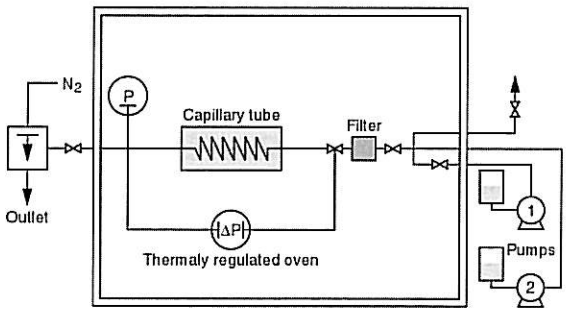


Fig. 1. Experimental device for the tube blocking test (TBT).

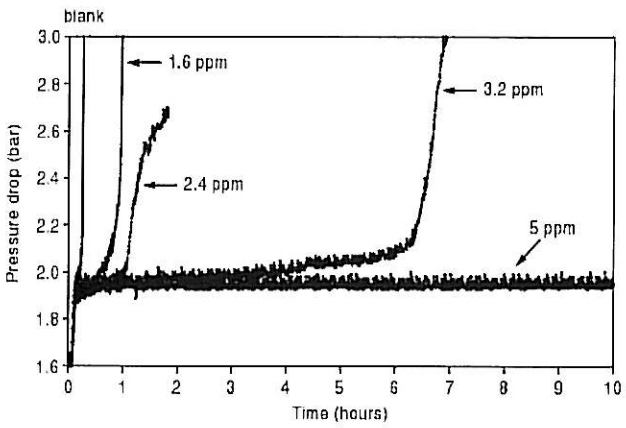


Fig. 2. MIC determination by the TBT method.

and Table 5 show the results obtained with these inhibitors. It can be seen that based on TBT results the inhibiting efficiency of green inhibitors is usually lower than that of phosphonates or polyacrylates.

Determination of Squeeze Lifetimes

Core flood experiments aim at defining the retention of the inhibitor during the injection of the inhibitor slug

Table 5. Comparative MIC of tested inhibitors.

Inhibitors	MIC $CaCO_3$ (ppm)
Phosphonate Dequest 2010 (HEDP)	< 4
Polyacrylate Romax 7200	2 < MIC < 5
Polyaspartates Baypure DS 100 MS 10 ter (lab IFP)	5 2,5
Polysaccharides Dequest PB CMPS 2.5 DP 10 " DP 24 CMPS 2.0 DP 10 DP 24 CMPS 1.5 DP 10	5 < MIC < 10 7.5 < MIC < 10 < 10 7.5 10

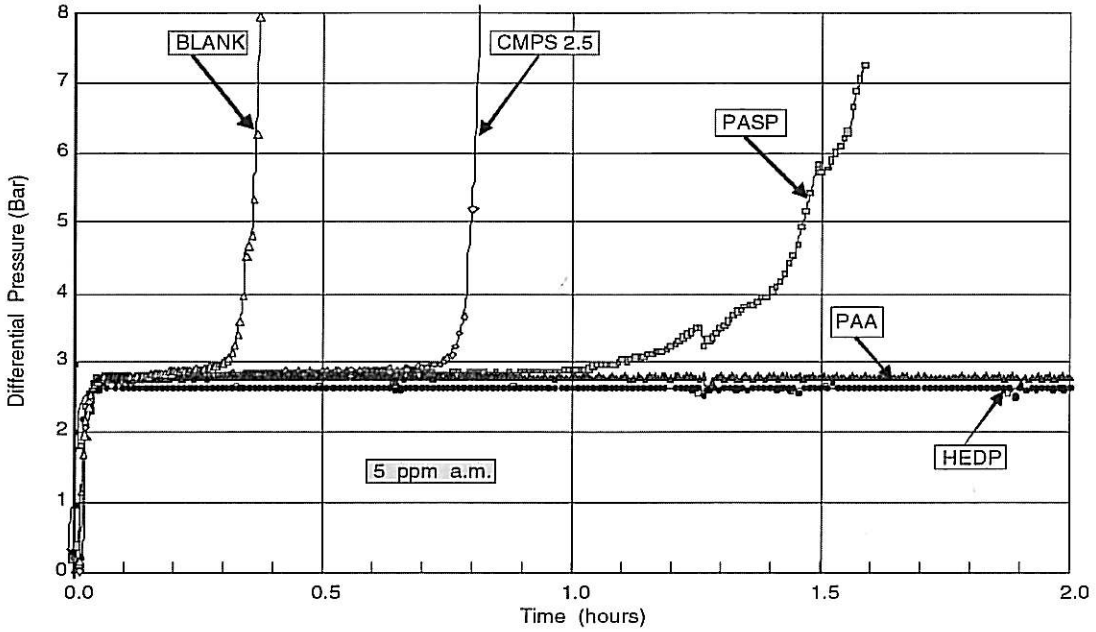


Fig. 3. Comparison of inhibitors by TBT, (C_{inh} = 5 ppm, 50/50 water mixture, 60° C).

and then the release of the product when the produced water is flushed into the core. The squeeze lifetime is determined from the released concentration and is defined as the number of pore volumes (PV) of water that can be flooded while keeping the inhibitor concentration higher than the MIC.

The squeeze lifetime measured in the experiment will be scaled to the well situation by numerical simulation (see below). To run the near wellbore simulations the inhibitor adsorption isotherm is required. The adsorption isotherm is calculated from the results of the core flood experiment performed at 100% water saturation.

The core flood involves mounting a reservoir core in a Hassler type flow cell placed in an oven at reservoir temperature (Fig. 4). The core is saturated with synthetic brine whose composition is representative of the produced brine. However, to avoid the precipitation of calcium carbonate and possible sulphates in the core, bicarbonate and sulphate ions are replaced by chloride ions. The sequence of injection involves the following steps: (1) injection of several pore volumes of the produced water for core conditioning and permeability measurement; (2) injection of three pore volumes of the inhibitor solution, at 10 g/l (active matter) dissolved in the injection water followed by overnight shut–in for inhibitor adsorption; (3) formation water back-production until the inhibitor concentration drops below the MIC (2.5 ppm active content). During the flood the differential pressure across the core and the pH are continuously recorded. The inhibitor concentration in the effluents is measured with the Hach method for the organo-

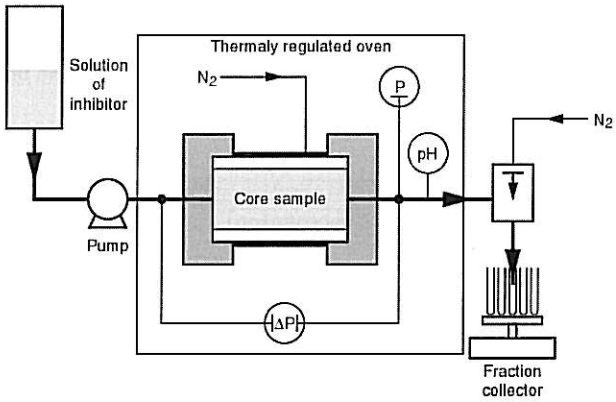


Fig. 4. Experimental device for core flood tests.

phosphonate and the ferrocyanide method for the polyacrylate[4].

Figures 5 and 6 show the inhibitor return with the produced water for the organo-phosphonate and the polyacrylate respectively. For the organo-phosphonate, the concentration in the effluents rapidly declines to 10 ppm active after ~ 80 pore volumes of brine injected, followed by a long tail region. The concentration drops to the MIC after ~ 300 PVs are injected but remains higher than 1 ppm active after 800 PVs of production. For the polyacrylate, the laboratory squeeze life time is much shorter than for the organo-phosphonate. The MIC is reached after the injection of only 40-110 PV of produced water.

Evaluation of Formation Damage

The formation damage is evaluated from the pressure difference across the core. Strong formation

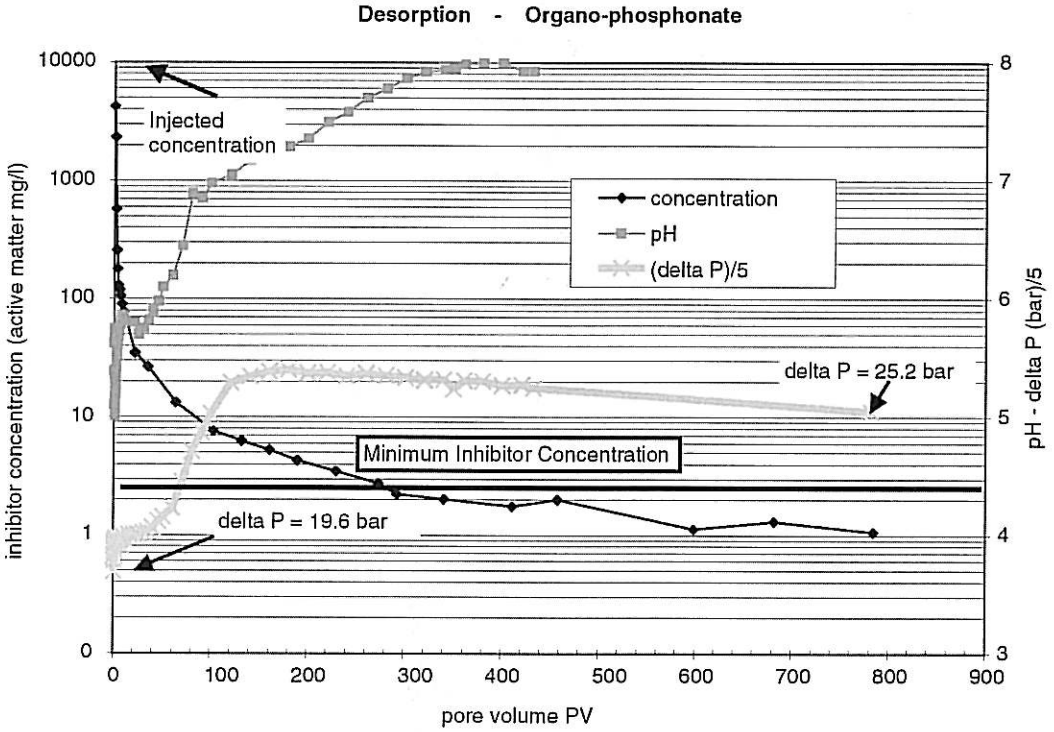


Fig. 5. Results of the core flood experiment: Inhibitor concentration in the effluent during water back-production, pH and ΔP as function of PVs injected. The inhibitor is an organo-phosphonate.

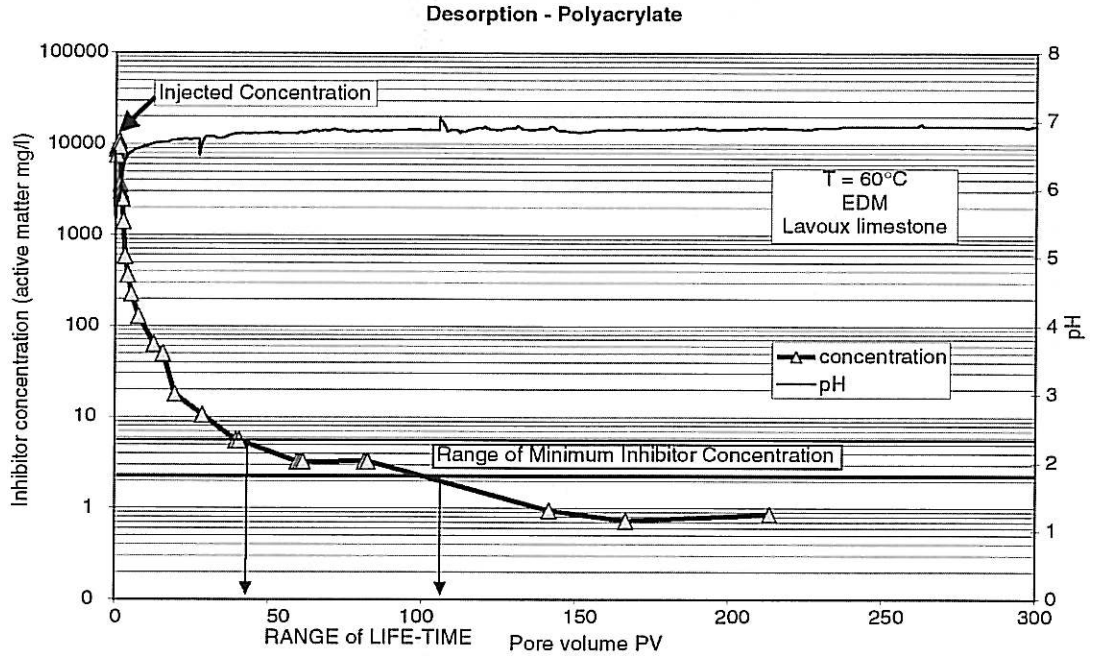


Fig. 6. Results of the core flood experiment: Inhibitor concentration in the effluent during water back-production, pH and ΔP as function of PVs injected. The inhibitor is a polyacrylate.

damage is observed with the organo-phosphonate whereas no damage at all occurs with the polyacrylate inhibitor. These differences are supposed to be due to the precipitation of the organo-phosphonate as explained below[5-7]. During the desorption stage of the organo-phosphonate (Fig. 5), the differential pressure rises significantly after 100 PV and then slowly declines. The increase of the differential pressure corresponds to the increase of the pH at values higher than neutrality. This feature is probably due to an unexpected precipitation of the phosphonate inhibitor during the early stage of back production. The precipitation behaviour is suspected to be due to the low solubility of the organo-

phosphonate at neutral pH and/or to the formation of an inhibitor/calcium complex with calcium cations released by carbonate dissolution. Note that this precipitation behaviour occurs at low inhibitor concentrations, which is consistent with the limited solubility of this type of product in the low concentration range. The precipitate partly re-dissolves during the flood, and the permeability after ~ 800 PV of back production is two thirds of the permeability at the end of the inhibitor injection stage.

Summary of Laboratory Tests and Choice of the Best Inhibitor Product

At this stage, the laboratory tests show that the organo-phosphonate is the best inhibitor in terms of squeeze lifetime: the low MIC and the high retention capacity of the core makes the desorption profile favourable with a slow release of the inhibitor concentration. On the other hand, the polyacrylate has a low retention capacity, although its MIC is of the same order of magnitude. The only drawback for the organo-phosphonate is the precipitation behaviour which causes permeability reduction and formation damage. Remedial treatment against formation damage is absolutely necessary before re-squeeze of this product.

MODELLING OF THE TREATMENT

The organo-phosphonate is the inhibitor selected from the laboratory tests. The procedure used for the calculation of squeeze life time in the well is based on core flood experiments. The current procedure consists of the calculation of a dynamic adsorption isotherm[8]. Even if precipitation is observed, it is supposed that the process almost certainly goes through an adsorption stage. The level of inhibitor in the return curve is then thought to be due to the desorption either by a chemical or a physical mechanism.

The adsorption isotherm, $\Gamma(C)$, is calculated from the propagation velocity V_C at a given concentration:

$$V_c = V_{fluide}/(1 + (\rho/\phi)(\partial\Gamma/\partial c)_c))$$

The adsorption isotherm follows the Langmuir form:

$$\Gamma = \Gamma_{max}\, bc/(1 + bc)$$

The calculated isotherm shows the classical low concentration steeply-rising curve (Fig. 7). Once the isotherm has been derived, it can be validated by modelling the core flood (Fig. 8). The reasonable agreement between the calculated and the experimental results shows the validity of the

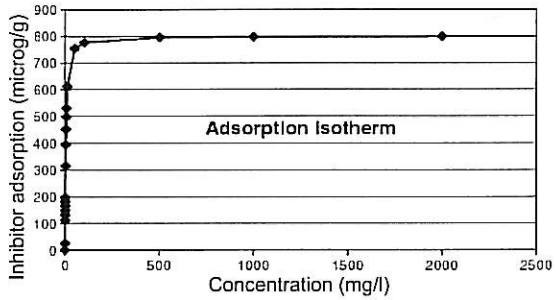


Fig. 7. Dynamic adsorption isotherm calculated from the results of the core flood experiment.

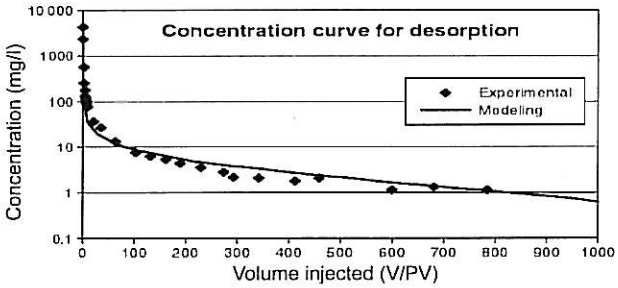


Fig. 8. Validation of the adsorption isotherm.

modelling. The interpretation of the results shows that in the threshold concentration region corresponding to the MIC (2.5 ppm active content), the amount adsorbed represents only 62 % of the inhibitor quantity retained in the porous medium. This means that 38% of the product remains available for a subsequent treatment when the MIC is reached.

The wellbore scale modelling is done with an in-house reservoir simulator SARIP^{CH} [9]. The treatment consists in the injection of the following sequences: (1) a pre flush to condition the near wellbore with the make-up brine for the inhibitor solution; (2) the inhibitor slug; (3) a post flush to allow a deeper penetration of the chemical into the formation; (4) a shut-in period for inhibitor adsorption[10]. The simulator does not calculate stage (4) since adsorption is modelled as an equilibrium, i.e. instantaneous, process.

A homogeneous radial 3-D model is used to simulate fluid behaviour around the wellbore. Inputs of the simulation are: (1) well geometry and petrophysics data, (2) water and oil properties, (3) inhibitor properties, i.e. MIC and adsorption isotherm, (4) rock type and permeability data, (5) conditions at the beginning of the treatment. During the well treatment, the fluid properties are assumed to be constant. The treatment design is optimised to reach a one-year lifetime given the MIC of 2.5 ppm active content. The duration of each of the treatment sequence (pre-flush, slug, and post-flush) is optimized given injection constraints.

The injection of 1000 bbl of inhibitor at 4000 ppm active matter fulfils the MIC requirement (Fig. 9). The

inhibitor concentration in the well effluents stays above the MIC limit. The concentration profiles (Fig. 10) are computed during the well production period. After a sharp drop in inhibitor concentration right at the start of the production (between 0.2 and 0.5 days), the concentration profiles are stabilised and smoothly decrease with time. The concentration profiles in the reservoir around the wellbore show that the treatment protects about 1.5 m around the well over the required one-year period.

In this paper, the simulation results presented are based upon homogenous reservoir properties. However, we recognise, in a complementary study, the influence of permeability heterogenities on squeeze inhibitor treatment.

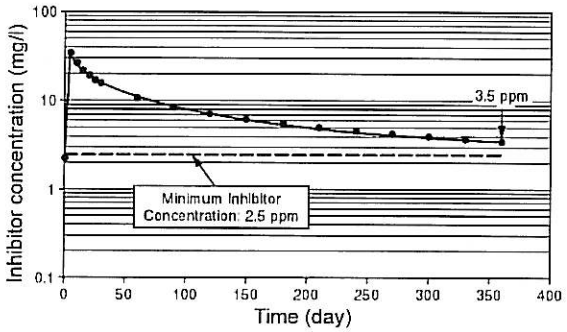


Fig. 9. Returned inhibitor concentration calculated at the producing well.

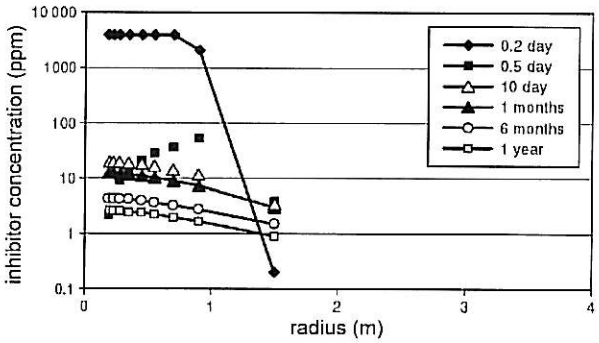


Fig. 10. Inhibitor concentration calculated by SARIP[CH] in the near well-bore region.

CONCLUSIONS

An integrated methodology including laboratory experiments and numerical simulations is presented for the design of an inhibitor squeeze treatment. The inhibitor efficiency is evaluated by Jar Tests and Tube-Blocking Tests. The two methods give a good agreement for the value of the MIC. The core flood test shows that the inhibitor is retained by an adsorption/precipitation mechanism for the organo-phosphonate. Transient formation damage is observed during the water back-production. Formation damage is not observed with the polyacrylate. However, the squeeze lifetime is very short. The laboratory data are integrated in a reservoir simulator for the modelling of the squeeze treatment on the well. A one-year lifetime treatment is obtained by the injection of a reasonable quantity of inhibitor.

REFERENCES

[1] Parkhurst, D. and Appelo, C., 1999. PHREEQC (version 2): a computer program for speciation, batch-reaction, one dimensional transport and inverse geochemical calculations, *U.S. Geol. Surv.*

[2] Kohler N., Pasquier D., Bazin B. and Lemaire C., 2003 (March). Selection of green inhibitors for squeezetreatments. Oil Field Chemistry Symposium, Geilo (Norway).

[3] NACE Standard Test Method TM0374-95: *Laboratory Screening Tests to Determine the Ability of Scale Inhibitors to Prevent the Precipitation of Calcium Sulfate and Calcium Carbonate from Solution (for Oil and Gas Production Systems).*

[4] Graham, G.M., Sorbie, K.S., Boak, L.S., Taylor, K. and Blilie, L., 1995 (February). Development and application of accurate detection and assay techniques for oilfield Scale inhibitors in produced water samples. *SPE* 28997, SPE Int.Symposium on Oilfield Chemistry, San Antonio, Texas.

[5] Jordan, M.M., Sorbie, K.S., Ping Jiang, Ming Dong Yuan and A.C. Todd, 1994 (February). Phosphonate scale inhibitor adsorption/desorption and the potential for formation damage in reconditioned field core. *SPE* 27389, presented at the SPE Intl. Symposium on Formation Damage held in Lafayette.

[6] Oddo, J.E. and Tomson, M.T., 1990. The solubility and stoechiometry of calcium DETMP at 70° C in brine solutions at pH 4.7 and 5.0. *Applied Geochemistry*, **5**, 527.

[7] Browning F.H. and Fogler, H.S., 1993 (March). Precipitation and dissolution of calcium-phosphonates for the enhancement of squeeze lifetimes. *SPE* 25164 presented at the Intl. Symposium on Oilfield Chemistry held in New Orleans, LA.

[8] Sorbie, K.S., Todd, A.C., Thornton, A.R. and Wat, R.M.S., 1992 (September). The interpretation and theoretical modelling of inhibitor/tracer corefloods. *SPE Production Engineering.*

[9] Le Thiez, P. and Lemonnier, P., 1990. An in-situ combustion reservoir simulator with a new representation of chemical reactions. *SPE Res. Eng.*, **9**: 285-292.

[10] Heinrichsen, C.J., 1998. Preventing scale deposition in oil production. *National Association of Corrosion Engineers* (NACE), paper N° 61.

Petroleum Res. J. Vol. 17 (2005); P. 81–86.

Demulsifying Power of Salts of Sulfated Ethoxylatated Nonylphenol and Their Combination with Certain Petroleum Sulfonates

Imad H. AL- Wahaib*, Mahmoud F. Farhat ** and A.A. Obeid ***

قدرة أملاح نونيل فينول المتكبرتة الأثوكسالية على الاستحلاب وامتزاجها مع سلفونات زيت بترول محددة

عماد وهيب ومحمود فرحات والصديق عبيد

لقد تم في هذا البحث دراسة تأثير ادخال مجموعة كبريتات في جزيّ مستحلب ايثوكسيلات نونيل فينول على فعاليته في ازالة الاستحلاب. وقد أظهرت أملاح الصوديوم للأثير المحتوي على مجموعات الكبريتات المحضر قدرة عالية على ازالة الاستحلاب . ويناقش البحث أيضا ظاهرة مزج هذه الأملاح مع سلفونات بترولية ذات وزن جزئي منخفض تم تحضيرها بسلفنة زيت غاز فراغي.

Abstract: *The influence of the introduction of a sulfate group into a molecule of nonylphenol ethoxylate emulsifier on its demulsification activity was studied. A great demulsifying power was shown by sodium salts of the produced sulfated ether. The feature of combining these salts with a low molecular weight petroleum sulfonate, obtained via sulfonation of a vacuum gas oil, is discussed .*

INTRODUCTION

The Efficiency of ethoxylated alkylphenols as demulsifiers to break crude oil emulsion is a function of both the alkyl side chain length and polyglycol chain length (number of ethylene oxide groups - nEO)[1,2]. The greatest demulsifying power was shown by the ethoxylated alkylphenols with C_9 - C_{12} alkyl side chain of (nEO) of about 20. The introduction of a sulfate group into two molecules of an ethoxylated alkylphenols has a significant effect on surface and demulsifying activities. The sulfate group in its influence of surface activity was found to be equivalent to approximately five moles of ethylene oxide, while in its influence on demulsifying activity was equivalent to 7-10 moles of ethylene oxide depending on crude oil nature[2].

In an investigation on the effects of crude oil components on demulsifying efficiency[3], it was noted that petroleum surfactants have marked effects on demulsifying power of a block copolymer of ethylene oxide .

The present work deals with the influence of the introduction of a sulfate group into a molecules of nonylphenol ethoxylate (NPE) emulsifier on its demulsifying activity. The feasibility of formulating a demulsifier combination containing a salt of sulfated NPE together with a low-molecular weight petroleum sulfonate, was studied as well .

* Chemistry Department, Faculty of Science, Omar Muchtar University, AL Baidha, Libya . Email: ialwahaib@ hotmail.com
** Chemistry Department, Faculty of Science, AL-Fateh University,Tripoli, Libya. Email:Mf_farhat @ yahoo.com
*** Chemistry Department, Faculty of Science, Misurata University, Libya. Email:Al Sedig@ hotmail .com

EXPERIMENTAL

The Sodium Salt of Sulfated NPE + H_2O

The preparation of this surfactant, starting with NPE emulsifier, consists of two steps; sulfation of NPE and neutralization of the sulfoether with caustic soda[2] according to the following reactions

$RC_6H_4(OCH_2CH_2)_nOH + H_2SO4 \rightarrow RC_6H_4(OCH_2CH_2)_nOSO_2OH + H_2O$

$RC_6H_4(OCH_2CH_2)nOSO_2OH + NaOH \rightarrow RC_6H_4(OCH_2CH_2)_nOSO_2ONa + H_2O$

Thus, the sufation was carried out with concentrated sulfuric acid taken in molar ratios of 1:1 -1:3 at a temperature of 40 °C for 2 hours . The resulting sulfated mass was diluted with acetone and neutralized with 30% caustic soda solution to phenolphthalein end point.

The acetone solution of the sulfoether, together with the sodium sulfate precipitated in the residue, was dried with anhydrous sodium sulfate, after which the sodium sulfate was filtered off, the acetone was driven off from the filtrate, and the residue was brought to a constant weight.

The Petroleum Sulfonate

This sulfonate product was prepared starting with vacuum gas oil of Az zawiyah Refinery. The group-chemical composition, determined by adsorptive chromatography on silica gel, showed that it contains 47.5% by weight aromatic hydrocarbons. The gas-oil was sulfonated with gaseous SO_3 , diluted with nitrogen at 55°C. The amount of reacted SO_3 was 1.2% by weight of the gasoil, corresponding to approximately 13% degree of sulfonation . The sulfonated gasoil had a content of sulfonic acids of 7.5% by weight. After neutralization with 10% aqueous caustic soda, the reaction mass was treated with aqueous isopropyl alcohol to extract the petroleum sulfonate .

Demulsification Properties

The change in emulsification properties of surfactants was evaluated via determining the stability of a direct emulsion, formed using toluene and water in a ratio of 20:80 and containing same concentration of different surfactants. The stability was evaluated by measuring the time needed for complete separation of the two phases at room temperature[4].

RESULTS AND DISCUSSION

Table1 includes results of the influence of molar ratio of NPE: concentrated sulfuric acid on the content. A high degree of purity of sodium salts of sulfated NPE was achieved using the molar ration of 1:3.

Table 1. Sulfation of NPE by concentrated H_2SO_4 at 40 °C.

NPE : H_2SO_4	Contents of sulfated NPE
(molar ratio)	in the products (wt.%)
1:1	55.1
1:3	95.2

The changes in emulsification properties of NPE, due to introducing sulfate group in the molecule, can be seen from the data of Table 2 .

Thus, in the presence of NPE as the surfactant, a highly stable emulsion was formed. However, a partial or complete replacement of this surfactant by the sulfated one caused a great decrease in stability of the direction of mono hydrophile surfactant.

Elucidation of the influence of incorporating the petroleum sulfate in the demulsifier composition was done using a product containing 65.4% by weight of sodium sulfonate, the remaining being unreacted

Table 2. The changes in emulsification properties of NPE as a result of its sulfation.

Surfactant	Concentration of the surfactant in the aqueous phase (wt.%)	Stability of 20:80 (toluene\water emulsion) (hours)
NPE	0.5	>24.0
NPE	1.0	>24.0
70% NPE+30% salt of sulfated NPE.	1.0	6.0
30% NPE+70% salt of sulfated NPE.	1.0	1.8
Salt sulfated NPE	1.0	1.5

gasoil, and having a surface activity value of 210 erg. $1/cm^2$ .g.

Results showed that a composition containing 80% of salt of sulfated NPE and 20% of the petroleum sulfonate exhibited higher demulsifying power than showed by any of the component taken separately.

REFERENCES

[1] Thalberg K. and Lindman B., 1991. *Surfactants in Solution* , Plemum press, New York,

[2] Gordnov V. P, Sorokin, V. V. and Petrol, A. A. P., 1974. *Chem.tech. Fuel Oil*, 4, 281.

[3] Makhonin G. M., Petrove A. A. and Borisov S. I., 1983.*Chem.. Tech. Fuel Oils*, 8, 410.

[4] MP joint QC-PDS, 1991. Stability committee. *Pharmaceutical Technology,* **15**, 92.