THE IMPACT OF CORROSION ON OIL AND GAS INDUSTRY

M B Kermani and D Harr

BP International, Sunbury on Thames, UK

This Paper was originally presented as SPE 29784 at the 1995 SPE Annual Technical Conference and Exhibition, held 11-14 March 1995 in Bahrain

ABSTRACT

The impact of corrosion on the oil industry has been viewed in terms of its effect on both capital and operational expenditures (CAPEX and OPEX) and health, safety and the environment (HSE). To fight against the high cost and the impact of corrosion within the oil industry, an overview of topical research and engineering activities is presented. This covers corrosion and metallurgy issues related to drilling, production, transportation and refinery activities.

INTRODUCTION

The wide ranging environmental conditions prevailing in the oil and gas industry necessitates the appropriate and cost effective materials choice and corrosion control measures. The implementation of these measures are becoming increasingly important as the impact of corrosion on safety, economy and the environment takes up more challenging roles. Furthermore, production conditions tend to become more corrosive hence requiring a more stringent corrosion management strategy.

Corrosion related failures constitute over 25% of failures experienced in the oil and gas industry. More than half of these failures are associated with sweet (CO₂) and sour (H₂S) producing fluids. An analysis of failures ascertained during the 1980s in a very limited industry wide survey, showed the degree of damage caused by corrosion and other types of materials degradation¹. An overview of these figures are given in Tables 1 and 2. These figures, to a lesser or greater extent, are equally applicable to the petroleum industry wide activities. It is apparent that corrosion imposes a significant cost penalty on the choice of material at the design stage and its possible occurrence also has serious safety and environmental implications.

Corrosion has a wide ranging implications on the integrity of materials used in the petroleum industry. Examples of these ranging from drilling, production, transportation and refinery are given in this paper - the examples are by no means exhaustive and implications of corrosion causing other forms of degradation such as those related with welding are not covered.

COST OF CORROSION

The impact of corrosion on the oil industry can be viewed in terms of its effect on both capital and operational expenditures (CAPEX and OPEX) and health, safety and the environment (HSE). Quantifying the cost of corrosion in these categories is not an easy task. Nevertheless, a recent in-house survey on the cost of corrosion to the BP Group presents a fairly comprehensive examination of such costs; and in general terms provides a valuable insight into the relative breakdown of likely corrosion costs affecting operators within the industry.

It is widely recognised that corrosion is a costly problem. These costs typically represent in any one year roughly 3% of Gross Domestic Product (GDP) for developed countries. If this is translated directly on to a company's balance sheet, as a percentage of turnover, then it represents a major cost in any one year.

There are four main ways in which corrosion costs can be incurred:

- Design expenditure or CAPEX; costs incurred at the project stage, representing
 additional capital outlay on preventing, minimising or controlling corrosion,
 compared to the expenditure that would have been required if corrosion did not exist.
 For example, capital expenditure due to corrosion on North Sea projects undertaken
 by BP in the 1980's averaged about 8% of total project CAPEX.
- Operating expenditure or OPEX; day-to-day costs associated with corrosion control and repair and including planned/unplanned maintenance costs as a result of corrosion damage. For example, in 1988 between 25% and 33% of maintenance costs of BP's oilfields in the UK Continental Shelf were corrosion-related
- Replacement expenditure; costs incurred in replacing/repairing major pieces of corroded plant and equipment where replacement/repair would be classified as capital expenditure. For example, the cost of replacing the Forties main oil fine riser failed in 1987 as a result of severe corrosion was \$11.5M.
- Lost revenue; costs associated with lost production, spoilage/contamination of products, or the "costs" of deferred cash flow due to delays in production caused by corrosion-related problems. For example, lost revenue due to the 18 days shutdown to replace the Forties riser in 1987 was estimated to be about \$5M.

It is also common to categorise corrosion costs in terms of "avoidable" and "unavoidable". Savings under "avoidable" costs may be realised by better use of existing or currently-available technology together with greater corrosion awareness and education. By contrast, there are other types of "unavoidable" costs which currently have to be incurred because of the realities of the world in which we live.

It is important to note that the recognition of an "unavoidable" corrosion cost should not be taken to imply prevention of corrosion at any cost. In most cases there is a trade-off between initial costs and those subsequently incurred throughout the life of the project. Hence, "unavoidable" costs result from use of corrosion-control practices which minimise the cost of a project over its complete lifecycle.

Reduction of costs which are currently "unavoidable", or even "potentially avoidable", will depend on advances in technology, and thus present challenges for research and development (R&D).

A review of BP operations, conducted in 1988, revealed total corrosion costs in the region of 1.5% of turnover with, in principle, 15% of these costs falling under "avoidable"; the industry average is claimed to be in the 25 - 33% range. BP's experience suggests that "avoidable" costs appear to arise from the combination of a lack of readily available information (about the cost-consequences of corrosion

failures), variable quality of information dissemination, and in some instances a tendency to minimise initial capital outlay.

THE IMPACT OF CORROSION ON HSE

Whilst cost is an important consequence of poor corrosion control and awareness, of equal importance is the potential impact of corrosion on health, safety and the environment (HSE). If unchecked or poorly controlled, corrosion can seriously affect plant and equipment integrity as well as its serviceability. This raises the risk of leaks and discharges of often flammable fluids and gases which present a potentially serious health and safety hazard. Also such releases may well have unacceptable environmental properties and consequences both inherent to the fluids themselves and with the production chemicals added to aid processing and transport (e.g. scale inhibitors, demulsifiers, corrosion inhibitors).

The last 15 years has seen a heightened awareness of and sensitivity to the environmental impact of the use and subsequent discharge of industrial chemicals. In the case of the oil and gas exploration and production (E&P) industry the application of production chemicals - for example, corrosion inhibitors, scale inhibitors, biocides and demulsifiers - is now essential to the successful operation of most oil and gas fields, but with these there is the risk of their subsequent entry into the surrounding environment

The North Sea, as a case in question, has been identified by the environmental organisations in many European countries as a system under great stress and at risk from pollution. Clearly the birth of the offshore North Sea oil industry in the mid 1970's and its resulting exponential growth has added to such concerns. Whilst environmental controls were imposed with the commencement of oil production, they were almost entirely concerned with the risks of oil pollution: for example, a level of 40 ppm maximum in water to be discharged is currently set.

The situation has now change significantly as governmental bodies have become better informed and are consequently invoking ever tighter controls, together with a far more "green" public consciousness.

Since 1982 a number of surveys have sought to describe quantitatively and qualitatively chemicals used and discharged into the North Sea from the E&P industry²⁻⁴. However, these have been far from conclusive on actual amounts of production chemicals discharged although total usage appears to directly reflect rates of oil and water production. Nevertheless, a key step was the Paris Convention addressing the prevention of marine pollution from land based sources, which came into force in 1978, where land based sources also encompasses man-made structures erected on the continental shelf of the North Sea. This has subsequently prompted a continuing effort to put in place an international system of environmental controls notably through the establishment of the Paris Commission (PARCOM)⁴.

Whilst the situation awaits a resolution, it is nevertheless clear that tighter legislation will emerge and its appropriateness is more regularly challenged. The three primary aspects of biodegradation, bioaccumulation and toxicity will undoubtedly be key criteria. Biodegradation is likely to apply to each component in a formulated product (e.g. corrosion inhibitor) expressed as the percentage that has decomposed after a fixed

period of time - typically 28 days. Bioaccumulation of each component addresses what fraction will partition into the cells of an organism. Toxicity of the total formulated product will be tested on organisms belonging to different trophic levels - primary producers (algae); consumers (fish); decomposers (sedimentary reworkers). In the case of the latter this may not only consider direct death (LC50) but also growth inhibition.

Clearly there is a balance to be struck between toxicity versus biodegradation versus bioaccumulation in defining the overall environmental acceptability of a product for a given application. This is being addressed through the CHARM (Chemical Hazard Assessment and Risk Management) scheme⁵ which is an Oslo/Paris Commission driven initiative. Acceptance of the environmental risk evaluation model is still being debated but until clear criteria are in place it leaves the E&P industry, and the chemical supply companies in particular, unclear as to what product acceptance and development should be based.

HSE concerns also apply to coatings where there is a drive to reduce their volatile organic compounds (VOCs) content and a move to high solids or more water based paint system. There has also been concerns raised about the use of zinc anodes for offshore use given the toxicity of zinc.

CORROSION IN DRILLING OPERATIONS

In recent years, the premature, and sometimes catastrophic, failure of drill string components has become an increasingly important consideration in drilling engineering design and research. Many cases of critical component failure have been experienced in applications where failures had not been encountered previously. In addition, increasingly complex designs and more stringent demands have been sought on the load carrying components of drill string. These failures occur more frequently in directional wells and contractors are seldom aware of the problem until a washout or a twist off occurs^{1,6,7}. The failures impose cost penalties to the oil and gas industry in the form of lost rig time, damaged tubular goods, necessary work-overs and abandoned or side-tracked wells.

Drill string failures result predominantly from cracks initiated at the fast engaged thread of made-tip tool joints⁶ schematically shown in Figure 1. Typically, most of these failures are caused by a corrosion fatigue process. Basic conditions necessary for such failures are present in drilling operations. Cyclic tension, torsion and bending are available and more importantly, the presence of drilling fluids and downhole vibration, assist in the formation and growth of corrosion fatigue cracks thus leading to failures. Even though corrosion fatigue has been recognised as the cause of these failures for some time, it is only in more recent years that serious problems arising from these failures have been frequently encountered and has led to systematic studies^{1,6-8}. Downhole vibration can cause numerous drillstring failure problems which are outwit the scope of this paper⁹.

Whatever the cracking mechanism, it appears that the sequence of tool joint failure can be divided into two stages, namely crack formation and crack propagation. The former is caused by the susceptibility of tool joint steel to hydrogen embrittlement in the presence of drilling fluids¹. The sequence of crack formation and propagation are illustrated in Figure 2. Both stages of cracking are mechanically, physically and environmentally dependent. Great efforts and extensive studies on the subject have led

to the development of preventive and predictive measures aimed at minimising the incident of failure^{1,6-9}. Lack of sensitivity of current inspection techniques is responsible for loosing sight of these cracks - recent development of alternative inspection techniques would lead to better detection of these cracks hence reducing the incident of failure^{1,7,10}. Crack propagation is caused by an appreciably lower fatigue strength of tool joint steel in the presence of drilling fluid, which facilitates growth of these cracks through a corrosion fatigue and finally a pure fatigue process⁶. Better predictive capability in crack propagation rate leads to improved knowledge of drillstring fatigue performance. The combination of better inspection technique and knowledge of crack propagation rate leads to better definition of necessary frequency of inspection allowing failure free operation.

PRODUCTION FACILITIES

In the context of production facilities, corrosion problem is exemplified by describing the significance of H₂Scontaining environments in the choice of production tubing and corrosion fatigue in marine structural steels.

Production Tubing - Sour Service Conditions

The appropriate choice of materials for well completions in sour fields is an important factor in the economic success of oil and gas activities. The choice is governed by mechanical properties, resistance to both corrosion damage and sulphide stress cracking (SSC), availability and cost.

Resistance to SSC is often the principal factor affecting the choice of materials for H₂S containing environments, since the occurrence of SSC² can result in a catastrophic and potentially hazardous failure associated with a hydrogen embrittlement mechanism. This is becoming increasingly important as wells are drilled deeper and downhole conditions tend to become more corrosive, with higher levels of hydrogen sulphide. This often necessitates the selection of highly alloyed, highly priced materials. Therefore, it is important to identify the mechanism of cracking and a method of assessing candidate materials so that the most cost-effective choice can be made.

For SSC to occur, a combination of tensile stress and an environment containing hydrogen sulphide is required. Hydrogen sulphide has a dual role in such cases; firstly it results in a lowering of the pH of the environment and secondly it catalyses the penetration of atomic hydrogen into the material ¹¹. Therefore, it is apparent that both solution chemistry and mechanical factors are the governing parameters in the performance of materials in sour service conditions. The former is a prerequisite for the availability of hydrogen at the metal surface, the latter enhances hydrogen diffusion

In deference to the foregoing, it is apparent that factors which promote hydrogen embrittlement would in turn affect the SSC behaviour of materials. These include factors which affect hydrogen availability, entry and its transport within the metal lattice. Thus the solution chemistry, as portrayed by its acidity, can govern the performance of materials in sour environments. Solution acidity in the presence of sulphide ions (sour environments) both facilitates the hydrogen evolution reaction, making it the dominant cathodic reaction, and enhances the amount of hydrogen absorbed within the lattice, thus increasing the degree of susceptibility to SSC.

Therefore, a knowledge of solution chemistry, and in particular the in-situ pH, can lead to the establishment of the SSC performance of materials. This in turn leads to a better definition of materials suitability for sour service exposure.

Bearing in mind the limitations of NACE MR0175¹² to address solution chemistry, new limits of sour service have been developed for a range of carbon and low alloy steels as well as corrosion resistant alloys. These have led to the development of plots correlating solution pH with H₂S partial pressure in a domain type relationship¹¹ shown in Figure 3. The plot has been divided into three main domains, each characterising the materials suitability for sour service applications with respect to their SSC behaviour. These domains are designated by the terms 'Non-sour", 'Transition" and "Sour". The domains characterise the suitability of different materials and tubular goods. Based on these domains, it is possible to identify the appropriate environmental conditions most relevant to the service limits of steels most frequently used for completion tubing. This approach has led to the selection of the most suitable and cost effective materials for sour service applications¹³.

Marine Structures

Many large marine, fixed gas and oil production platforms are constructed from low strength marine structural steels. These structures are subject to cathodic protection in order to prevent their general corrosion. Maintenance of such structures and their long term integrity require the ability to understand the effect of cathodic protection on their mechanical performance and a full knowledge of fracture mechanics. The ability to predict corrosion fatigue behaviour of marine structural steels is of prime importance in life prediction and reliability assessment of offshore structures. The fatigue performance of these C-Mn steels when stressed in saline solutions has been the object of intensive studies in the recent years 14-16. These data have demonstrated that the presence of saline environments increases the fatigue crack growth rates (FCGR) over the values measured in air by a factor of 2-4, but the degree of enhancement is dependent on both the stress intensity range and the cathodic protection level as shown in Figure 4.

The influence of cathodic potential is explained on the basis of the build-up of hydrogen at the crack tip. It can be speculated that the two competing processes in this situation are hydrogen build-up or its availability at the crack tip and the effective crack tip strain rate in developing freshly created metal. Hydrogen entering the metal lattice at the crack tip via freshly created surfaces, builds up to a concentration sufficient to induce brittle cleavage fracture over a distance ahead of the crack tip, the extent of which is determined by the effective strain rate at the crack tip.

The acceleration in crack propagation rate results in a decrease in the predicted life of tubular joints 15-16 as shown in Figure 5 plotting corresponding stress range as a function of cycles to failure.

TRANSPORTATION FACILITIES

Corrosion is a natural potential hazard associated with oil and gas transportation facilities. This results from the fact that an aqueous phase is inevitably co-produced with the oil and /or gas. The inherent corrosivity of this aqueous phase is then heavily dependent on the level of CO₂ and H₂S acidic gases which are also co-produced. The

presence of H₂S, CO₂ and brine in crude oil not only give rise to increased corrosion rates, but also can lead to environmental fracture assisted by enhanced uptake of hydrogen atoms into the steel. Apart from the possibility of SSC in oil and gas transportation pipelines, absorption of hydrogen generated by corrosion of carbon steels in wet H₂S containing environments can have other adverse effects on the properties of steels. One adverse effect which has been observed in pipeline steels is the development of blisters and /or cracks along the rolling direction of the steel. These are associated with inclusions and segregations. The terms hydrogen induced cracking (HIC), hydrogen pressure cracking and hydrogen induced stepwise cracking are used to describe cracking of this type in pipeline steels. Another phenomena is that of stress orientated hydrogen induced cracking (SOHIC) which is facilitated in the presence of hoop stress. These issues are source of concern in the engineering application of steels, although mostly have been addressed extensively.

CO₂ Corrosion - Sweet Service Conditions

CO₂ is usually present in produced fluids and although it does not in itself cause the catastrophic failure mode of cracking associated with H₂S, its presence can nevertheless result in very high corrosion rates where the mode of attack is often highly localised (Mesa corrosion). In fact CO₂ corrosion, or "sweet corrosion", is by far the most prevalent form of attack encountered in oil and gas production. The problem of CO₂ corrosion has long been recognised and has prompted extensive studies¹⁷.

Dry CO₂ gas is itself not corrosive at the temperatures encountered with oil and gas production, it needs to be dissolved in an aqueous phase through which it can promote electrochemical reaction between steel and the contacting aqueous phase. CO₂ is extremely soluble in water and brines; but it should also be remembered that it has even greater solubility in hydrocarbons - typically 3:1 in favour of the hydrocarbon.

CO₂ dissolves in water to give carbonic acid, a weak acid compared to mineral acids as it does not fully dissociate:

$$CO_2 + H_2O \Rightarrow H^+ + HCO_3^- \Rightarrow H_2CO_3$$

Whilst there is some debate about the mechanism of CO₂ corrosion in terms of which dissolved species are involved in the corrosion reaction, it is evident that the resulting corrosion rate is dependent on the partial pressure of CO₂ gas. This will determine solution pH and the concentration of dissolved species for a given temperature.

CO2 Corrosion Nomograms

A very simple "rule of Thumb" approach often cited in the industry in defining CO2 corrosion of carbon and low alloy steels is described in Table 3. This is based on field experience, principally in the US. No subsequent standard guidelines exist as to the courses of action necessary for each condition, although experience will trigger the corrosion engineer to initially look towards certain possible options.

Such a simplistic approach may be viewed as:

An aid to first pass materials selection

Offering qualitative and generalised assessment

More specific questions on service life, risk analysis, corrosion allowance, and inhibited corrosion rates require the ability to conduct a quantitative assessment i.e. the ability to predict corrosion rates for a given set of conditions. Consequently, the relationship between corrosion rate and CO₂ partial pressure has formed the basis of a number of predictive models/equations for carbon steels, where the most widely recognised and used of which is the de Waard and Milliams nomogram¹⁸.

A simplified version of the de Waard and Milliams equation together with the various correction factors is given in Figure 6. However, a more recent paper by the de Waard and Milliams¹⁸ gives a more exacting analysis to take better account of scaling (formation of Fe₃O₄ and/or FeCO₃ films) and water chemistry (resulting in pH buffering). Scaling of the steel surface can result in a degree of passivation such that the corrosion rate may become acceptably low, and is dependent on temperature, CO₂ partial pressure and water chemistry/degree of iron ion saturation. The scale correction factor is only applied in low salinity waters (usually associated with gas wells, typically ≤0.1% NaCl equivalent) and for many situation is only necessary at temperatures > ca. 60°C.

It is worth remembering that the de Waard and Milliams equation was originally developed for application to wet gas conditions based on laboratory test data, although it is now commonly applied to conditions also associated with crude oil production: its weakness lies in its inability to adequately account for the effect of flow on corrosion and particularly film/scale stability.

A more pragmatic approach which places direct emphasis on knowledge of the water chemistry is that of Crolet¹⁷ which defines severity in terms of low, medium or high risk. Their approach takes into consideration not only predicted potential corrosion rate but also in situ pH, Ca²⁺/HCO₃, concentration of dissolved organic acids (notably acetic acid), velocity and, more importantly correlation with field experience. The risk assessment is run on a spreadsheet (CORMED).

There are even more detailed models developed, but use of either the de Waard and Milliams or CORMED approach is for many situation sufficient to enable determination of the worst case potential corrosivity and hence suitability of carbon or low alloy steels (plus corrosion inhibitor) or the need to move to higher metallurgy¹⁷. However, it must be remembered that these models/equations are not strictly valid in the presence of H₂S due to formation of protective sulphide films which may nevertheless be susceptible to localised breakdown under long term exposure. Figure 7 sets out a process for determining CO₂ corrosion risk/rate. In achieving this, a key element is the interaction between the corrosion engineer and the petroleum engineer to ensure that the service conditions are correctly defined and relevant.

Whilst CORMED does attempt to address the effect of flow on corrosion, this generally remains a grey area in the predictive process. It is not only flow velocity that needs to be determined, but also flow regime which for multi or mixed phase fluids will determine whether water wetting of the steel surface will occur. Clearly if continuous hydrocarbon wetting is occurring, then the corrosion risk will be extremely low. Key factors here are oil/water ratio and emulsion tendency/stability. For many crude oils the

presence of a water cut > ca. 35% will lead to water becoming the continuous phase for a fully mixed oil/water system such that corrosion then becomes a continuous potential risk. Similarly if the Gas/Oil Ratio (GOR) is > 5000 then continuous water wetting can be expected.

Figure 7 includes a general approach to the consideration of flow in assessing the overall risk of CO₂ corrosion. The flow parameter currently favoured for determining the effect on corrosion rate and film formation/stability is liquid shear stress at the pipe wall. This can be fairly readily calculated using available commercial software. However, it must be recognised that for specific situations it may be necessary to conduct laboratory tests under simulated flow conditions. Laboratory testing becomes particularly critical where erosion due to the presence of particulates is a concern. There are no industry guidelines which adequately cover this situation. The commonly cited API RP-14E recommended practice strictly refers to pure gas-in-liquid induced erosion (i.e. no particulates present) and applies the basic formula:

$$V_e = constant / (density)^{1/2}$$

where V_e is the limiting fluid velocity above which erosion will occur. The relationship is essentially empirical as is the value of the constant used for a given material; this is more often than not based on individual operator experience. For example, BP currently uses 135 for C-steel, 200 for 13% Cr steel, and 235 for Duplex Stainless Steels accepting that these are still conservative figures. The computed V_e can then be readily translated into a liquid shear stress. Although there is limited reported data on upper limits regarding shear stress, a figure of 100 Pa for C-steel above which erosion becomes a problem is considered by some as appropriate.

REFINERY

Several natural constituents present in oil can cause corrosion of refinery equipment. These constituents include sulphur compounds, salt water, inorganic and organic chlorides, organic and inorganic acids and nitrogen which forms cyanides. Extensive research has led to recommendations in the appropriate use of alloys and corrosion control methods for these applications. Refinery facilities in contact with H₂ at high temperatures and pressures may suffer from hydrogen damage. Because atomic hydrogen diffuses readily in the steel, cracking may result from the formation of CH₄ at high pressures in internal voids in the metal. This results in internal fissuring at grain boundaries plus decarburisation with loss of strength which may lead to equipment failure. In this respect the use of chromium and molybdenum steels has been shown to improve the resistance to hydrogen damage. Steel development has offered improved strength properties and the vanadium modified steels also have much enhanced resistance to hydrogen damage. Also, improved and sensitive monitoring of damage has led to more accurate analysis of the safe remaining life of components¹⁹.

DISCUSSION AND SUMMARY

The impact of corrosion is essential in reducing industrial incidents, minimising the impact on the environment and responding to demands for the use of 'greener' products. Pollution prevention is an important element of corrosion engineering principals.

Responsibility for HSE is becoming increasingly recognised as serious as that for any other operating practice that affect performance in the petroleum industry.

In achieving the ultimate target of a safe and environmentally acceptable operation and reducing the high cost of corrosion, a systematic and responsive corrosion management strategy needs to be put in place. The lifecycle of corrosion management strategy embraces inception, design, development, implementation, monitoring and inspection. This all encompassing strategy by the use of appropriate and fit-for purpose technology enables safety of operation, optimisation of materials and service with HSE issues in mina. Successful implementation of corrosion management strategy would depend on the use of a responsive monitoring and inspection system backed by close communication between corrosion engineer, production chemist, inspection personnel and petroleum or plant engineers - hence corrosion management is not a function that should be managed separately from business operations.

Significant number of studies on the cause and type of corrosion in the petroleum industry have been carried out. The outcome of these studies, in addition to assisting the recognition of the corrosion mechanism, has provided important practical implications through distinguishing cost effective materials choice and effective preventive and predictive measures to minimise this insidious type of failure.

In the search for new sources of oil and gas, operational activities have moved to harsher environments in deeper high pressure/high temperature wells and deep waters yet challenged by economy, materials integrity and prediction of long term performance. These are key issues requiring a systematic approach to research and development, success of which depends on a close dialogue between all those involved.

Some of the current understanding of the impact of corrosion in petroleum industry have been described. It is apparent that many questions remain unanswered particularly those associated with the exact nature of CO₂ corrosion.

In drilling operation, premature fatigue failures of drilling string components has become an increasingly important consideration in drilling engineering design and research. Predictive and preventive measures to reduce the likelihood of failure are key factor to successful drilling operations.

In production activities, deep water exploitation is essential in search for the new sources of hydrocarbon. This introduces a major challenge in materials engineering which requires sophisticated structural designs together with high integrity medium strength steels.

Transportation of crude oil and wet natural gas has posed considerable attention in recent years particularly for the development of marginal fields. A cost effective and appropriate corrosion strategy with respect to the selection and utilisation of corrosion inhibitors, corrosion monitoring and inspection techniques is vital for the economic viability.

The approaches presented for the selection of materials for sweet and sour duty highlight the need to give relevant consideration to solution chemistry, particularly the in-situ pH, for design in sour service environments, and flow regime for design in sweet service conditions.

The SSC domain relationship leads to three distinct regions of performance, each characterising a range of materials which can confidently be used in H₂S containing conditions. It is apparent that in evaluating material suitability for sour service applications, solution chemistry has to be addressed appropriately. Therefore, in situations where solutions are not extremely acidic, more economical materials can be selected with confidence. This methodology is in contrast with that recommended by NACE¹¹. The NACE recommended procedure is based on a wide range of operational experience and field data prior to 1975 and relies on false protection afforded in oil wetted surfaces. This recommendation can invariably lead to very conservative choice of materials in some cases with an attendant cost penalty. Furthermore, test results produced in the acidified sodium chloride solution recommended in NACE TM0177 cannot truly represent field conditions and again lead to very conservative materials choice.

With the growing environmental awareness and imposed international legislation, corrosion issues within refineries are becoming increasingly prominent requiring focused and intensive engineering activities.

ACKNOWLEDGEMENT

Authors wish to thank BP Exploration for permission to publish this paper.

REFERENCES

- Kermani, M B, "Hydrogen Cracking and its Mitigation in the Petroleum Industry", The Proceeding of the Conference on Hydrogen Transport and Cracking in Metals, The Institute of Materials, London, in publication
- 2. Chemical Usage in the North Sea Oil and Gas Production and Exploration Operations", Report for the Norwegian Oil Industry Association (OLF) Environment Committee, C M Hudgins, February 1990.
- 3. A Study for UKOOA on the Voluntary Notification Scheme for the Selection of Chemicals Used Offshore", Technical, November 1988.
- Report of the Paris Commission (PARCOM) on the Use and Discharge of Production and Exploration Chemicals in the North Sea Oil Industry" 1987.
- CHARM: An Environment Risk Evaluation Model for Offshore E&P Chemicals", P M Schobben, M C Th Scholten, E A Vik, S Bakke, Phase I Report, TNO, Den Helder (Netherlands) and Aquateam A/S (Norway), 1994.
- Kerrnani, M B, 'Drill String Threaded Connections; Failure Analyses and Case Studies', Proc International Conference on Fatigue of Large Threaded Connections, pp 35-56 eds. W D Dover, 1989.

- 7. Da l e, B A, 'An Experimental Investigation of Fatigue Crack Growth in Drillstring Tubulars', Proc. SPE Technical Conference, New Orleans, LA, SPE 15559, 1986.
- Gonzalez-Rodriguez J G and Procter R P M, 'Environmental Cracking of AISI 4145 Steel in Drilling Muds', Advances in Corrosion and Protection, ed. R P M Procter, pp 515-520, 1993
- Payne, M L, Abbassian, F and Hatch, A J, "Drilling Dynamic Problems and Solutions for Extended Reach Operations", ASME, ETCE, Houston, Texas, Ian. 1995.
- Topp, D, "The Use of Manual and Automated ACFM Technique for Subsea and Topside Crack Detection and Sizing", Offshore South East Asia, 10th Conference and Exhibition, Singapore, pp. 281-288, 6-9 Dec. 1994.
- Kermani, M B, Harrop, D, Truchon, M L R and Crolet, J L, 'Experimental Limits of Sour Service for Tubular Steels', NACE Annual Conference, CORROSION '91, Paper No 21, Cincinnati, Ohio, 1991.
- 12. 'Sulphide Stress Cracking Resistant Metallic Materials for Oilfield Equipment' NACE Standard MR0175-94, 1994.
- Kermani, M B, Mardn, J W and Waite, D F, 'Hydrogen Sulphide Cracking of Downhole Tubulars', Proc. SPE Technical Conference, Bahrain, SPE 21364,1991.
- Procter, R P M, 'Cathodic Protection Theory and Practice the Present Status', Coventry, Paper No 18, 1982.
- Kermani, M B and Abbassian, F, 'Corrosion Fatigue of Marine Structural Steels in Saline Environments', Proc. 12th International Corrosion Congress, Paper No 327, Houston, 1993.
- Dover, W D and Dharmavasan, S, 'Fadgue Fracture Analysis of T and Y Joints, Proc. 14th Annual Offshore Technology Conference, OTC 4404, Houston, 1992.
- "Predicting CO2 Corrosion in the Oil and Gas Industry", eds. M B Kermani and L M Smith, European Federation of Corrosion Series, No 13, 1994.
- 18. de Waard, C and Milliams, D E, NACE Annual Conference, CORROSION '91, Paper No 577, Cincinnati, Ohio, 1991.
- Liaw, P K, Saxena, A and Schefer, J, 'Predicting the Life of High Temperature Structural Components in Power Plants', Journal of Metals, pp 4348, February 1992.

TABLE 1

ANALYSIS OF SELECTED NUMBER OF FAILURES IN PETROLEUM RELATED INDUSTRIES

Type of failure	Frequency (%)
Corrosion (all types)	33
Fatigue	18
Mechanical damage/overload	14
Brittle fracture	9
Fabrication defects (excluding welding defects)	9
Welding defects	7
Other	10

TABLE 2

CAUSE OF CORROSION RELATED FAILURE IN PETROLEUM RELATED INDUSTRIES

Type of failure	Total failure
CO ₂ related	28
H ₂ S related	18
Preferential weld	18
Pitting	12
Erosion corrosion	9
Galvanic	6
Crevice	3
Impingement	3
Stress corrosion	3

TABLE 3

RULE OF THUMB CO2 CORROSION OF CARBON & LOW ALLOY STEELS

Condition	Corrosivity
P _{CO2} < 7 psi (0.5 bar)	Corrosion Unlikely
7 psi (0.5 bar) < P _{CO2} < 30 psi (2 bar)	Possible corrosion
P _{CO2} > 30 psi (2 bar)	Corrosion

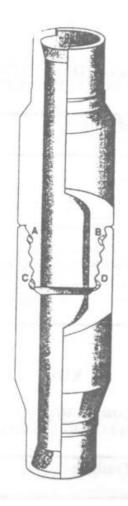


Figure 1. Critical locations for fatigue cracking of drillstring threaded connections.

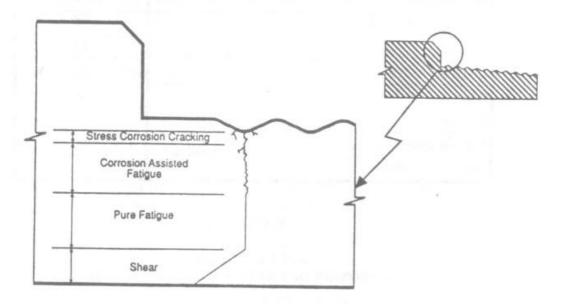


Figure 2. Cracking of drillstring tool joint.

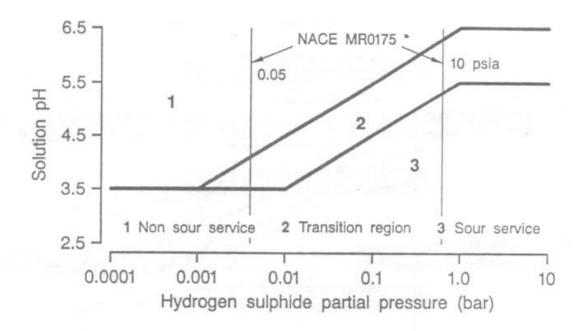


Figure 3. Limits of sour service.

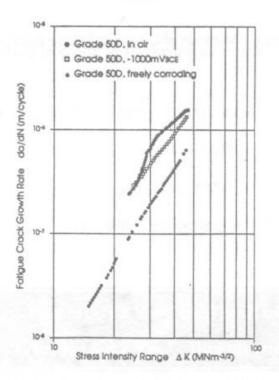


Figure 4. Fatigue crack growth rate of Grade 50 steel in aerated 3.5% NaCl solution (at R=0).

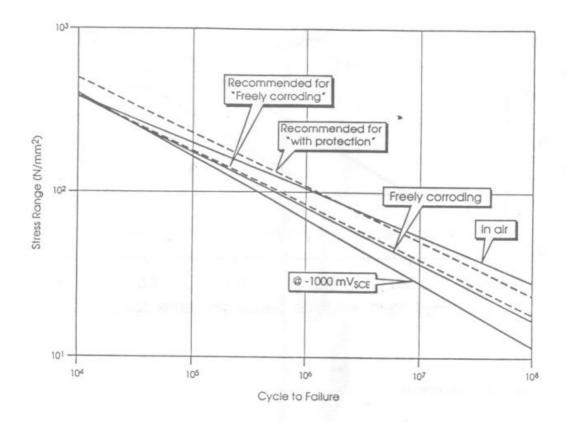


Figure 5. Corresponding Stress - Number of Cycles to failure (S-N) curves.

```
Basic Equation: \log_{10} (V) = 5.8 - 1710/(t + 273) + 0.67 x \log_{10} (P<sub>CO2</sub>)

Scale Factor: \log_{10} (F<sub>S</sub>) = 2400/(t + 273) - 0.6 x \log_{10} (f<sub>CO2</sub>) - 6.7 (Apply for T > 60 °C)

pH Factor: \log_{10} (F<sub>pH</sub>) = -0.13 x (pH<sub>actual</sub> - pH<sub>calc</sub>)<sup>1.6</sup>

pH<sub>calc</sub> = 3.71 - 0.5 \log_{10} (f<sub>CO2</sub>) + 0.00417 x t
```

```
Corrosion Rate (gas) = V \times F_s (mm/y)
Corrosion rate (oil) = V \times F_{pH} (mm/y)
```

Figure 6. de Waard and Milliams equations for calculating CO_2 corrosion rate; where V is corrosion rate (mm/y), t is temperature (°C), f gas fugacity factor and P_{CO2} is CO_2 partial pressure (bar).

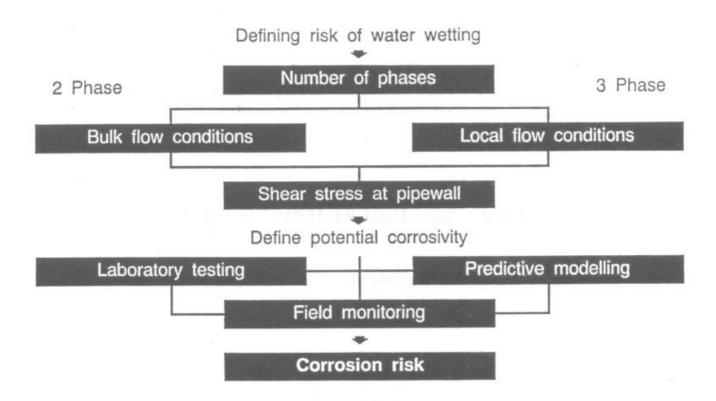


Figure 7. The procedure in defining CO₂ corrosion risk.