Corrosion Inhibitor Guidelines

A practical guide to the selection and deployment of corrosion inhibitors in oil and gas production facilities

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## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Summary</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>Acknowledgements</strong></td>
<td>7</td>
</tr>
<tr>
<td><strong>Introduction</strong></td>
<td>9</td>
</tr>
<tr>
<td><strong>System Design and Commissioning</strong></td>
<td>11</td>
</tr>
<tr>
<td>Why Use Carbon Steel + Corrosion Inhibitor?</td>
<td>11</td>
</tr>
<tr>
<td>Corrosion Engineering Design</td>
<td>15</td>
</tr>
<tr>
<td>The Value of Pre-Start-Up Internal Epoxy Coatings for Carbon Steel Pipelines</td>
<td>16</td>
</tr>
<tr>
<td>Hydrostatic Testing and Commissioning of Carbon Steel Lines</td>
<td>17</td>
</tr>
<tr>
<td>Keypoints</td>
<td>20</td>
</tr>
<tr>
<td><strong>Corrosion Inhibitor Selection</strong></td>
<td>23</td>
</tr>
<tr>
<td>Choosing a Batch Treatment Corrosion Inhibitor</td>
<td>23</td>
</tr>
<tr>
<td>Choosing a Corrosion Inhibitor for Continuous Treatment</td>
<td>26</td>
</tr>
<tr>
<td>Oil/Water Partitioning of Corrosion Inhibitor</td>
<td>36</td>
</tr>
<tr>
<td>Deciding Field Dose Rate</td>
<td>41</td>
</tr>
<tr>
<td>Compatibility Issues</td>
<td>41</td>
</tr>
<tr>
<td>Environmental Issues</td>
<td>44</td>
</tr>
<tr>
<td>Keypoints</td>
<td>46</td>
</tr>
<tr>
<td><strong>Deployment</strong></td>
<td>49</td>
</tr>
<tr>
<td>Oil Company/Chemical Company Alliances</td>
<td>49</td>
</tr>
<tr>
<td>Quality Control of Corrosion Inhibitor Supplies</td>
<td>51</td>
</tr>
<tr>
<td>Corrosion Inhibitor Pumping Problems</td>
<td>52</td>
</tr>
<tr>
<td>Injecting Inhibitor into the Process Stream</td>
<td>54</td>
</tr>
<tr>
<td>Corrosion Monitoring</td>
<td>56</td>
</tr>
<tr>
<td>Dealing with Process Changes</td>
<td>56</td>
</tr>
<tr>
<td>Dealing with Process Interruptions</td>
<td>60</td>
</tr>
<tr>
<td>Responsibilities</td>
<td>61</td>
</tr>
<tr>
<td>Keypoints</td>
<td>62</td>
</tr>
<tr>
<td><strong>References</strong></td>
<td>65</td>
</tr>
<tr>
<td><strong>Index</strong></td>
<td>69</td>
</tr>
</tbody>
</table>
These guidelines cover all aspects of inhibitor deployment including why they are used, how they are selected, and how to achieve maximum performance in the field to alleviate internal corrosion of facilities. This type of information is often passed on verbally amongst personnel in oil companies and inhibitor suppliers and is not formally recorded or summarised in any reference book. Consequently, the authors of this document carried out an extensive series of interviews with staff from BP, inhibitor suppliers, and other oil companies (Shell, Elf, Conoco, Statoil, Phillips, Norsk Hydro and Arco) to try and gather as much accumulated experience as possible. We have now collated all the information and present here a summary of industry views on corrosion inhibitors together with our recommendations on best practises. The main conclusions are summarised by the bullet points below. More examples and industry opinions are given within the document.

**System Design and Commissioning**

- Many corrosion problems arise from poor facilities design (e.g. probe locations, injection points) or poor interpretation of the design during installation. Corrosion engineers should be involved in the front end engineering design, at least to review proposals.

- Corrosion resistant alloys (CRAs) are used increasingly at production sites, e.g. 13%Cr steel has become a virtual standard for downhole use where CO$_2$ corrosion is a concern.

- Carbon steel is still economically favoured for long pipelines particularly because of its lower initial capex.

- Non-metallic materials such as glass reinforced plastics and plastic lined carbon steel pipe offer potentially major cost savings but are yet not well proven for production duties.

- Drying the process stream (gas or oil) will prevent carbon steel corrosion. By itself this approach can be risky for oil lines and it is more reliable to use chemical corrosion inhibitors.

- Low-build internal epoxy primer coatings for carbon steel pipelines are often considered a cost-effective way to minimise internal corrosion until production starts and corrosion inhibitor injection begins, but they do not give long term corrosion protection.
Hydrotest water should always contain at least two treatment chemicals; oxygen scavenger and a compatible biocide. An $O_2$ corrosion inhibitor is only necessary if the oxygen scavenger might be consumed by the atmosphere during dosing.

Corrosion inhibitor should be dosed from day 1 of operation because one can never be sure that the process stream is completely dry.

**Corrosion Inhibitor Selection**

- Corrosion inhibitor squeezes into the reservoir are uncommon. As much as two-thirds of the inhibitor may be “lost” and, due to its surfactant nature, there can be reductions in well productivity.

- Batch treatment inhibition is not fully understood and can not be used confidently until various uncertainties are removed, in particular, doubts about the persistency of the inhibitor film after lay down. Continuous treatment is universally preferred amongst the oil and chemical companies we contacted.

- Batch treatment is only suitable when the application is non-severe, when continuous treatment is technically difficult (e.g. downhole in gas wells, remote locations) or when batch and continuous treatment are used together for severe or upset conditions.

- A batch or continuous inhibitor which performs well in one field may be inefficient in another under different conditions. Therefore, it is wise to check the performance beforehand in lab tests.

- A full corrosion inhibitor selection programme in the laboratory is an efficient way to choose a product. However, laboratory testing is only ever an approximation of real conditions and so it gives approximately the best products. These must then be further assessed in the field.

- The BP selection strategy for continuous corrosion inhibitors has evolved over more than ten years. A shortlist of products is narrowed down through a series of solubility tests, static and dynamic corrosion tests, and water/oil partitioning runs.
The main purpose of a partitioning test is to estimate the inhibitor dose rate required on total fluids. For example, a product may show good efficiency at 25 ppm in water-only tests, but 60 ppm may be needed in a water/oil mixture in order to reach the same efficiency.

Due to the many components in proprietary corrosion inhibitor packages and also measurement artefacts, partitioning should be regarded as a qualitative concept - as in “preferentially water soluble” or “preferentially oil soluble” - rather than a numerical constant to be used for extrapolating to different conditions.

The dose rate determined in the lab should be introduced in the field and then gradually reduced or increased to an optimum value using field monitoring. However, cutting the operational dose rate is sometimes regarded as a soft target for cost savings. It should be done carefully in order to avoid undesirable repercussions.

Field corrosion monitoring must be effective and reliable before an operator can confidently justify a reduction in dose rate, especially by a large amount.

It is essential to check the compatibility of a corrosion inhibitor with every material, lining, seal, and oilfield chemical with which it is likely to come in contact. Incompatibilities of any sort can cause serious operational problems.

Environmental concerns are increasingly likely to influence the selection of all types of oilfield chemicals. To date there has been some evolution towards environmentally friendly corrosion inhibitors but not yet any definite legislation to enforce it or recommendations to guide it.

**Deployment**

Alliances or contracting relationships already exist in many important oilfield areas so it is no surprise that such arrangements are now being introduced more widely for the
selection and deployment of oilfield chemicals. There are potential advantages and disadvantages in this trend.

- Only those suppliers meeting a recognised quality standard such as ISO9000 should be used. A simple performance test on every batch of corrosion inhibitor is a useful precaution easily accommodated by suppliers.

- Pump problems can be due to both poor design and poor operation. Many of the operational problems (e.g. bad calibration, inhibitor supply exhausted) can be avoided through good procedures and training.

- The corrosion inhibitor should be injected as far upstream as possible. This often means at the wellhead in order to protect process equipment already known or predicted to give a corrosion problem (possibly certain bends or tees).

- Injection immediately downstream of the final stage oil/water separator is appropriate if the separation process might be upset by corrosion inhibitor, if large amounts of corrosion inhibitor are likely to be lost with the separated water, and if the corrosion inhibitor is primarily intended to protect an export pipeline rather than the processing equipment.

- The inhibitor must be added just upstream of a turbulent region (e.g. bend, valve, pump) or directly into a turbulent process stream to ensure good mixing.

- Typically the injection quill should be positioned midstream, facing against the flow (unless pigging requirements prevent it). Direct injection into any water phase is needed for laminar or stratified flow conditions.

- Corrosion inhibitor is often diluted in solvent for use in gas lines, downhole injection, and batch treatment. There must be adequate control over both the diluent and the dilution process.

- Field corrosion monitoring is covered in detail in a companion document.

- An immediate response to certain key process changes will reduce the corrosion risk. The inhibitor type and dose rate should be continuously matched to the process throughput,
water cut, CO\textsubscript{2} level, O\textsubscript{2} level, H\textsubscript{2}S level, pH and sand production.

- Process interruptions like shutdowns and acid returns require their own special set of precautions to prevent corrosion damage.

- It is essential to actively manage corrosion using a Corrosion Management Strategy with all parties having clearly understood accountabilities.

- Sharing information about corrosion experiences and near misses, both within BP and externally, often repays the effort required.
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Statoil
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These guidelines cover the deployment of corrosion inhibitors downhole, in flow lines, processing equipment, and export pipelines in large oilfields. The text covers all aspects of inhibitor use including why they are used, how they are selected, and how to achieve maximum performance in the field to alleviate internal corrosion of facilities. This type of information is not easily available elsewhere. Whilst corrosion inhibitors are described in textbooks and industry monographs (e.g. from NACE - the National Association of Corrosion Engineers; and various oilfield chemical companies) it is usually in fairly general terms. Much of the detailed, accumulated expertise on corrosion inhibitors for the oil and gas industries resides within the production companies and chemical suppliers. Often this is passed on verbally amongst personnel and is not formally recorded or summarised. In short, there is no existing written reference source for detailed information about corrosion inhibitor deployment.

This document is intended to fill the gap. We carried out an extensive series of interviews with staff from BP, inhibitor suppliers, and other oil companies (Shell, Elf, Conoco, Statoil, Phillips, Norsk Hydro and Arco) to try and gather as much experience and anecdotal information as possible. We have now collated all the information and present here a summary of industry views on corrosion inhibitors together with our recommendations on best practise.

The related issue of field corrosion monitoring is of particular interest at the moment. This is covered in the companion “Corrosion Monitoring Manual” document [1].

We found much common opinion on many corrosion inhibitor issues. However, there was also abundant evidence of the same expensive lessons being relearned over and over again. This report should help BP to avoid “reinventing the wheel” in the same way by making sure that important experience is quickly available to those making decisions about inhibitors. The information is intended to complement the detailed procedures listed in the Corrosion Management Systems already adopted or being developed by many BP assets.
There is an ongoing debate about the relative merits of corrosion resistant alloys (CRAs) and carbon steel + corrosion inhibitor (CS/CI) in the oilfield. Circumstances will differ from case to case and obviously must be considered individually. Nevertheless, it is interesting that opinions on both sides of the argument often relate to the technical backgrounds of those concerned. Metallurgists and Materials Scientists will usually promote the advantages of CRAs and the limitations of CS/CIs (e.g. “I don’t really believe in inhibitors”) whilst chemists will enthuse about the efficiency and flexibility of inhibitors (e.g. CI type and concentration). It is no surprise either that the inhibitor supply companies tend to take the latter view!

An objective view recognises advantages and disadvantages for both options. In the high temperature, high CO₂ downhole environment CS is highly vulnerable, CIs are difficult to deploy and have poor efficiency. 13%Cr has therefore become a virtual standard for downhole use for sweet corrosion, despite its higher cost. BP’s experience is certainly favourable [2]. 13%Cr usually works out cheaper than the many workovers normally required on carbon steel tubulars. CS/CI becomes a more technically viable option for process pipework and for in-field flowlines. However, concern about the effects of complex geometries, crevices and dead legs on CS/CI means that CRAs are often preferred for process equipment, especially offshore. For long (>5km), large diameter export lines CS/CI has significant capex advantages (see Box 1).

**Box 1: Relative Costs of Different Metals**

The details below are semi-quantitative only. Precise costs will depend on many factors such as location, timescale, quantity, dimensions etc.

The new 36 inch 180 km Forties main-oil-line installed cost was £160 million in 1987, the majority of which was for the carbon steel pipe. One can see how expensive a higher metallurgy would have been for this long pipeline. The costs of CRAs become more bearable for smaller quantities of material.
An intermediate option between CRA and CS/CI is to internally clad CS selectively with a thin layer of CRA [3]. This is often adopted for regions of high fluid velocity such as bends and tees.

The new generation of non-metallic materials (see Box 2) has so far been limited mainly to water duties and requires further development for production duties. Hence, overall, materials selection depends critically on location and the prevailing fluid conditions. Further information on selection is available in detailed documents describing BP’s current practises [e.g. 4].

**Box 2: Non-Metallic Materials Options**

Polymer based non-metallic materials offer a number of corrosion-free piping options all with particular capabilities and envelopes of operation [5]. Water service is already well proven and although oil production experience is more limited, this is likely to change as the industry becomes more accustomed to the new possibilities.

**GRP** - Glass Reinforced Plastic composites offer a number of benefits such as weight savings, no corrosion and reduced maintenance. The realisation of this potential has been slow but application of GRP is now beginning, for example on Phillips J Block and Ekofisk, Shell Brent and Draugen, British Gas Armada, and Amoco AMOSS. The applications are generally fire water mains and sea water cooling and - on AMOSS - tankage, gratings, ladders. However, the material is more brittle than steel and requires a completely different set of installation procedures. There are also concerns over temperature limitations, long term ageing effects and inspection difficulties.

**PCT** - Plastic Coated Tubing employs a thin epoxy coating on carbon steel (ca 100-200 micro-metres). The performance of PCT is very variable in both water injection and production service as a result of coating quality and damage. Joint sealing can be a problem, and gaps in the coating (“holidays”) are difficult to detect and repair.

**GRP lined pipes** - These comprise a GRP annulus bonded to the inside of a steel pipe using a ca 1 mm layer of cement grout. The pipes have screwed connection systems which are already used for downhole water injection tubing and are currently being developed and qualified for some pipeline applications, mainly in the USA. Effective sealing at the joints can be a problem.

**PE and PVDF liners** - Polyethylene polymer liners have long been used for land based water and wet gas service. They have now been used subsea for water injection and hydrocarbon service is likely to follow. The liner is installed onshore and fits tightly inside, though remains unbonded. It is ca 10-15 mm thick so that holidays are not a concern. Continuous lengths up to ca 1 km can be lined at one time so there is a joining problem to be overcome between sections during pipe-laying. Nevertheless, lined carbon steel offers cost savings over duplex and other high metallurgy options. Polyvinylidene Fluoride (PVDF) is a new material now being introduced for liners.

The capex advantage of CS/CI for long pipelines is important. Less money is required up-front during development of a field. Once it starts production the revenue generated can be used to cover opex costs. This situation is frequently preferred to specifying CRA which, although it may have a lower “whole life cost” (capex + opex), will still
require much higher up-front capex. There are a number of computer models in use which forecast lower “whole life costs” (or “net present values”) for CRA compared to CS/CI for both short and long pipelines. The comparison is complicated and requires assumptions about several unknowns such as the discount rate (depends on tax regime, interest rate, company strategy). Some of these models are generally available (e.g. NiDI [6], NACE) and some are in-house in the oil companies.

CS has some other advantages over CRAs. It is much more readily available in large amounts, from more sources, and in different dimensions (diameter, thickness etc). For example at least 5 years notice might well be required for a manufacturer to supply enough CRA for a major pipeline. Fabricators and contractors tend to have more experience of CS. It is also a versatile material. Its physical and mechanical properties can be varied over a wide range by small changes in composition. A particular advantage is the relative ease of welding during installation; welding time is a major factor in determining overall installation time, especially offshore. Generally, CS is easier to weld than CRAs, though there are exceptions: for example high strength carbon steels require great care when welding, especially in thick sections. Screwed connections may be attractive for CRAs with poor weldability. They have a good but not perfect record for 13%Cr downhole tubulars where occasional small leaks do occur but can often be tolerated until the next workover. In contrast, pipeline leaks often demand a shutdown in order to effect a satisfactory repair.

Although CRAs are much more resistant to general corrosion than CS they do have their own particular set of corrosion problems. When CRAs do corrode it tends to be in a localised rather than a general manner. Dissolved oxygen and high chloride concentrations are well known for causing CRA pitting. This can be a problem, for example, when a 13%Cr producing well is turned round to become a sea water injector. If sea water deaeration is inefficient then there is a real risk of oxygen induced pitting of 13%Cr downhole, as well as crevice corrosion at the connections. As another example, one North Sea operator lost many km of 13%Cr line due to severe pitting after hydrochloric acid flow back. CRA’s are also susceptible to stress corrosion cracking. Alloys with ferritic, martensitic or duplex microstructures are likely to have only limited resistance to sulphide stress corrosion cracking in sour environments. Alloys with austenitic or duplex microstructures may be susceptible to chloride ion stress corrosion cracking, particularly if they have been welded or cold worked and are exposed to high chloride low pH environments.

CS has many advantages but unfortunately it does corrode readily in many environments. Coatings are effective for external protection of
pipelines, often backed up by cathodic protection (CP). This protection is more difficult internally due to problems of application, quality control and the risk of coating delamination and erosion (see Box 3). Furthermore, conventional CP will not protect internal surfaces. One viable alternative for major pipelines is to dry the process stream since water is needed to support corrosion reactions. Dry gas export pipelines are still fairly common. The prevailing temperature along the whole length is kept above the water dew point so that no aqueous liquids will condense. However, the increasing trend offshore is to operate with unmanned or limited facilities at the wellhead and this requires transport of wet gas.

Some operators use drying for crude oil streams (to <0.5%v/v water) backed up by regular pigging to remove any accumulations of residual water. This can be a high risk policy if corrosion monitoring is poor. It is only really appropriate if the pipeline corrosion allowance can accommodate high corrosion rates for the lifetime of the oilfield.

In a wet gas line a buffer such as sodium bicarbonate (NaHCO₃) or diethanolamine (DEA) can be added to raise the pH to a less corrosive value, > ca 6 (i.e. “gas buffering”). However, the most common approach to controlling CS corrosion in wet gas and wet crude oil streams is to use chemical corrosion inhibitors. There can be problems here too but the rest of this document is aimed at discussing these problems and recommending best practises. Some operators have used CS/CI successfully for 15-20 years in crude oil export pipelines in the North Sea.

**Box 3: Coatings**

One can not rely entirely on internal coatings for long term corrosion protection in oilfield production pipework. Major problems can include coating "holidays" (ie gaps), delaminations and bad joints (creating preferential corrosion damage), and general poor wear performance (making the coating susceptible to damage by pigging, wireline, sand impingement etc). Gas export lines have been coated to reduce pressure drop but corrosion inhibitors have still been employed to protect bare metal at welds and areas of damaged coating.

However, internal pipeline coatings are used to protect pipewalls during laying and hydrotesting. BP have used a thin epoxy primer layer, typically 50 microns thick, which just covers the peaks on a grit blasted surface. This British Gas idea adds around 5% to the cost and has been used on Forties, Miller, Emden, Brae, and Prudhoe pipelines. The coating is not "high build", and is not present at field welds. It is resistant to blistering, flaking and pigging but over a period of time it will wear away at the metal peaks thereby exposing more of the surface.

Process vessels on produced water duty are often made of carbon steel and are protected by a combination of cathodic protection (CP) and a bottom-half or a complete coating of, for example, glass flake epoxy. In such applications, inspection and repair is more straightforward than for pipe internals. However, QA during application is still a major problem which may mean that CRAs are cheaper in the long term.
Corrosion Engineering Design

The design of most oilfield facilities in BP follows the traditional sequence of,

- feasibility
- statement of requirements - SOR
- front end engineering design - FEED
- engineering procurement, installation, construction - EPIC

At one time all of this would have been done in-house but now more and more is being handled by contractors with BP defining the initial scope and then maintaining a supervisory or, increasingly, a partnership role. Corrosion engineers are currently involved mainly in the feasibility and SOR phases. They help to choose the optimum material and, if it is CS, will also specify an appropriate corrosion allowance to be used in the FEED phase. A corrosion prediction model such as the well known de Waard and Milliams approach is likely to be used in this work if CO\textsubscript{2} is present in the process stream. This model has now reached its fifth or sixth revision\textsuperscript{[7]}. It is conservative in predicting the general CO\textsubscript{2} corrosion rate (i.e. it overestimates the general corrosion rate) but it has underestimated the localised corrosion measured in certain BP locations. This is possibly because the local conditions have not been fully accounted for, are not known, or are outside the scope of the model. However, de Waard and Milliams has not yet been supplanted by anything more accurate and it remains a reasonable and well proven starting point for design.

Insufficient attention to corrosion engineering design during FEED can lead to problems. The classic example is the location of corrosion monitoring probes. Many people we interviewed spoke with dismay about the number of access fittings they’d encountered which were useless, perhaps as many as 70%. Some were sited on the bottom of pipe (six o’clock position) but with insufficient clearance below to allow probe insertion or removal. Some were placed at the 12 o’clock position in low velocity, low water cut lines. It was as if these fittings had simply been inserted neatly on the process drawing without any thought as to their purpose. Retrofitting new access fittings is rarely a convenient remedial measure. BP Recommended Practice RP 6-1 on “Corrosion Monitoring” describes the locating and fitting of probes\textsuperscript{[8]}, however, the advice to use a 12 o’clock orientation is not always appropriate. In most situations the probe should be oriented so that it will experience the water phase.
The installed location of corrosion inhibitor injection points has also led to problems, e.g.,

- An injection point was sited just upstream of a “tee” and in operation the inhibitor was preferentially swept into one branch but not the other. Injection points were actually required on both lines downstream of the “tee”.

- A single corrosion inhibitor injection pump delivered chemical into a manifold which was linked to several flow lines at a production site. The flow rate of chemical into each wellhead depended on the respective well pressures so that some wells received a lot of inhibitor and some virtually none.

- Several onshore wellheads had their own injection points but no electrical power available to operate a local injection pump.

- On one North Sea platform the corrosion inhibitor delivery line led into a platform drain rather than a process pipe.

These kinds of design/installation errors can cause major problems during operation. They could be avoided by proper attention to, and awareness of corrosion issues during the FEED and installation phases.

The Value of Pre-Start-Up Internal Epoxy Coatings for Carbon Steel Pipelines

BP has used “low build” internal epoxy primer coatings for wet gas and wet oil lines in order to protect carbon steel linepipe during transport, installation and storage until production starts (Figure 2). The coating is not expected to give much protection in service, indeed, it is expected to be progressively worn away. Therefore, a full corrosion inhibitor deployment programme is still necessary. The epoxy coating simply complements this. In any case, the coating stops short of the pipe ends and so the welds are unprotected (welding would burn any coating off anyway). Inhibitor is certainly needed for those bare areas even if the rest of the epoxy does remain intact.

Some coating suppliers argue that this situation with a lower area of bare surface allows a lower corrosion inhibitor dose to be used. This is not true for a batch treatment corrosion inhibitor because some inhibitor will inevitably coat the epoxy. Neither is it true for a continuously injected inhibitor because the same inhibitor concentration is needed to protect one bare patch as to protect a
whole uncoated pipeline. The inhibitor efficiency is proportional to the bulk inhibitor concentration, whatever the surface area.

Applying the epoxy coat typically adds about 5% to the cost of the pipe for a major pipeline. However, the potential benefits are clear. There is much reduced risk of scrapping batches of stored pipe which have corroded badly due to puddles of water forming along the bottom. Operators gave us several examples of this for batches of uncoated pipe sitting at a supply base ready to go offshore. Even if there is no major penetration, enough pre-corrosion can occur to make some areas susceptible to general corrosion or pitting when in service. An epoxy coating overcomes this hazard and also aids protection when the line is full of hydrotest fluid awaiting start-up. Furthermore, the lack of substantial amounts of corrosion deposits reduces the risk of internal plugging and seat damage of pipeline valves. BP’s Forties replacement main-oil-line, Bruce export line, Miller gas line and Miller crude oil line have all successfully used epoxy coatings for pre-service protection. Ultimately it is designers and planners who must decide if the extra cost for epoxy is justified and, despite the above, some do feel that it is not cost-effective.

**Hydrostatic Testing and Commissioning of Carbon Steel Lines**

After installation all oilfield lines are pressure tested with a liquid, invariably water, to ca 1.25 times the service rating (i.e. hydrostatic testing). The water can be fresh or saline depending on what is available. Whichever is used it may remain in the pipe for up to 2 years before production starts and before corrosion inhibitor is added, although a period of a few weeks to a few months is more typical.
A simple approach has been used by one North Sea operator. A short sub-sea line was filled with fresh water adjusted to a pH >9 where carbon steel does not corrode. Other operators and suppliers recommend combinations of oxygen scavenger, biocide, corrosion inhibitor and dye. The recommendations range from oxygen scavenger alone through to all four components. Typical concentrations are shown in the table.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>ppm (in fresh or saline water)</th>
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<tr>
<td><strong>Oxygen Scavenger</strong></td>
<td></td>
</tr>
<tr>
<td>Short dwell time (up to 4 weeks)</td>
<td>125</td>
</tr>
<tr>
<td>Long dwell time</td>
<td>100-200</td>
</tr>
<tr>
<td><strong>Biocide</strong></td>
<td></td>
</tr>
<tr>
<td>Short dwell time (up to 4 weeks)</td>
<td>100-200</td>
</tr>
<tr>
<td>Long dwell time</td>
<td>200-500</td>
</tr>
<tr>
<td><strong>Corrosion Inhibitor</strong></td>
<td></td>
</tr>
<tr>
<td>Short dwell time (up to 4 weeks)</td>
<td>100</td>
</tr>
<tr>
<td>Long dwell time</td>
<td>500</td>
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<tr>
<td><strong>Dye</strong></td>
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oxygen scavenger: ammonium bisulphite (NH₄HSO₃) or sodium bisulphite (NaHSO₃) is normally used. Both operate as reducing agents,

\[
O_2 + 2HSO_3^- \rightarrow H_2O + 2SO_4^{2-}
\]

About 3 ppm NH₄ HSO₃ or NaHSO₃ (i.e. ca 5 ppm of 65% solution) are required to consume 1 ppm dissolved oxygen. Air saturated fresh water contains ca 10 ppm dissolved oxygen at 10°C, therefore, a 125 ppm scavenger dose rate is a ca 4 times overdose. This is required because there is likely to be some loss of scavenger to atmospheric oxygen, depending on how it is dosed. Some operators and suppliers feel that all the scavenger will be lost in this way and so it is not worth adding. They argue that the dissolved oxygen will be rapidly consumed anyway by corrosion inside the pipe. On the other hand some say that only oxygen scavenger is needed since, if the oxygen is removed, there will be no bug growth or corrosion.

biocide: This is not needed for very short dwell times, as long as these are assured. One operator had to abandon a line because of bacterial problems after omitting biocide from hydrotest water and then leaving it in place for a considerable time.
Eventually the hydrotest water must be discharged. This is normally done at the seaward end of the pipe in the case of an offshore line. In any location the treatment chemicals (biocide, oxygen scavenger, corrosion inhibitor, dye) must meet all the local environmental regulations. These regulations are becoming increasingly more stringent in many parts of the world. As a result manufacturers are actively developing more environmentally friendly oilfield production chemicals. However, the concept of an environmentally friendly biocide for hydrotests does sound peculiar. The description relates to the biodegradability of the product over a certain period, rather than its initial toxicity. The issue of environmentally friendly corrosion inhibitors is fully discussed later (see p.44).

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When the process facilities are started up for commissioning and then for full production there is a question over when to begin adding corrosion inhibitor. In the past some operators have not added CI until the water cut rose above a certain level (e.g. >1% water in a crude oil stream) reasoning that if there is no water then there’s no corrosion. While this is undoubtedly true the key point is whether one can ever really say that there is “no water”. Even if the average water cut is very low there is still a chance of droplets gradually wetting the steel surface and accumulating, perhaps augmented by sporadic slugs of water not picked up by routine monitoring. Corrosion will then occur, as some operators have discovered. We
were given a number of examples of this. Unfortunately the addition of CI at this stage has not always controlled the problem.

Most operators now seem to recognise that corrosion inhibitor should be added from day 1. In other words as soon as the hydrotest water has been discharged. The intention is to try and maintain inhibited fluids and a pristine steel surface at all times. Experience shows that once corrosion becomes established it can be difficult to eliminate or cost effectively control. Day 1 inhibition is especially advisable for sub-sea lines which are expensive, inaccessible and difficult to monitor. Inhibition is a prudent insurance policy to maintain safety and integrity. Monitoring and repair are less difficult on topsides or onshore facilities and so some operators do not add any inhibitor here until the measured water cut reaches a defined level. They rely on efficient inspection to give them early warning of any corrosion problem and then hope to respond quickly.

**KEYPOINTS: System Design and Commissioning**

- Many corrosion problems arise from poor facilities design (e.g. probe locations, injection points) or poor interpretation of the design during installation. Corrosion engineers should be involved in the front end engineering design, at least to review proposals.

- Corrosion resistant alloys (CRAs) are used increasingly at production sites, e.g. 13%Cr steel has become a virtual standard for downhole use where CO$_2$ corrosion is a concern.

- Carbon steel is still economically favoured for long pipelines particularly because of its lower initial capex.

- Non-metallic materials such as glass reinforced plastics and plastic lined carbon steel pipe offer potentially major cost savings but are yet not well proven for production duties.

- Drying the process stream (gas or oil) will prevent carbon steel corrosion. By itself this approach can be risky for oil lines and it is more reliable to use chemical corrosion inhibitors.

- Low-build internal epoxy primer coatings for carbon steel pipelines are often considered a cost-effective way to minimise internal corrosion until production starts and corrosion inhibitor injection begins, but they do not give long term corrosion protection.
Hydrotest water should always contain at least two treatment chemicals; oxygen scavenger and a compatible biocide. An O₂ corrosion inhibitor is only necessary if the oxygen scavenger might be consumed by the atmosphere during dosing.

Corrosion inhibitor should be dosed from day 1 of operation because one can never be sure that the process stream is completely dry.
Batch treatment and continuous treatment are the two main choices for corrosion inhibitor deployment. Each of these requires different selection tests so it is necessary to decide which will be used before starting the selection. The third deployment method is corrosion inhibitor squeezing.

A corrosion inhibitor squeeze is analogous to the more common scale inhibitor squeeze where the chemical is injected into the reservoir at the bottom of the well so it can leach slowly back into the wellbore fluids when production restarts. This requires that the chemical is sufficiently held back by adsorption onto the reservoir rock and therefore the approach is only viable for certain formations. The amount and degree of dispersion of the scale inhibitor in the reservoir is calculated so that the leach-back provides protection over an extended period. Squeezes are rarely used for corrosion inhibitors. They are expensive and as much as two thirds of the inhibitor may remain in the reservoir. This is less of a concern in scale inhibitor squeezes since many reservoirs actually require scale inhibition due to mixing of formation water and injected sea water. In contrast, no corrosion inhibition is ever required in the reservoir. The missing two thirds is simply wasted. Even when corrosion inhibitor squeezes have been carried out they can give poor results. Production rates have sometimes gone down due to reduced sand permeability, permanent skin damage and damaged gravel packs. These downhole effects are no surprise since corrosion inhibitors are normally surface active materials with the potential to alter the wetting properties of the reservoir. There is also a decreasing concentration profile for the inhibitor over time which requires careful monitoring and which will eventually demand that another squeeze is carried out. There are many drawbacks to squeeze treatment and, therefore, batch or continuous addition are better deployment options for corrosion inhibitors.

The small oil producers of West Texas are familiar with batch treatment. Tankers visit periodically and travel round each field pumping a few gallons of corrosion inhibitor down every well. The idea is to coat vulnerable surfaces with a film of inhibitor which will persist until the next scheduled treatment (see Box 5). For larger
scale operations, however, we found that continuous treatment was preferred universally amongst oil and chemical companies. Batch treatment was only recommended for remote sites with no power where there is little alternative; when the application was non-severe (e.g. low predicted corrosion rate in almost dry fluids); or when continuous treatment was technically difficult (e.g. downhole in gas wells, gas flow lines, large diameter gas export lines). As conditions become more severe the recommended deployment method changes from batch, to continuous, to batch plus continuous. One chemical company estimated that only 10% of their corrosion inhibitor business came from batch treatment products.

Box 5: Corrosion Inhibitor Mechanisms

The chemistries of batch and continuous treatment corrosion inhibitors are different, though the suppliers are vague about the precise details. Whereas continuous treatment inhibitors tend to form monomolecular films on the steel surface [11], batch inhibitors are designed to form thicker “macrofilms”. This is achieved by using mainly high molecular components which have only marginal solubility in the carrier solvent. When the mixture is washed by production liquids the carrier solvent is removed and the solute precipitates as an insoluble layer on the surface.

Estimates of initial film thickness (i.e. before washing with the production fluids) are required in order to calculate the volume of inhibitor needed to coat a certain surface area. Various rules of thumb exist specifying thicknesses of 0.001 - 0.004 inch. These figures apparently arise from unspecified studies in the paint industry and elsewhere. Simple coupon immersion tests at Sunbury using a commercial batch corrosion inhibitor gave a figure of 0.0006 inch.

When a batch inhibitor is applied in a pipeline as a slug between two pigs the pigs should be tight fitting so that the inhibitor is smeared onto the surface. Otherwise the inhibitor will simply flow out round the edges of the pig over a short length of pipe. Some operators preflush the system with methanol in order to clean up the surface and make it ready for the inhibitor.
The most common use of batch treatment is downhole in gas wells. Continuous treatment downhole can be difficult. Operators have had problems with corrosion of the injection strings, valve and connection leaks, and blocking of the string. In the new high angle wells it is physically difficult even to install a chemical injection string. An alternative approach is to fill the annulus with a large volume of inhibitor and allow it to run slowly into the produced fluids through a partially open valve above the packer. One operator tried this and eventually found out that the valve was only opening every 3 days. Also, filling the annulus means there is a large volume of inhibitor to handle and dispose of if it is found not to be performing.

Continuous dosing via the annulus has also been used during gas lift. Careful formulation is necessary for gas lift corrosion inhibitors in order to avoid the solvent flashing off at high downhole temperatures. This causes the viscous solute to “gunk” out on the annulus wall and fouling of the injection valves. High boiling solvents such as glycerol are required to avoid this. Such gunking can be a particular problem with combined corrosion inhibitor/scale inhibitors since water is often used in the formulation to dissolve the scale inhibitor component. This water will flash off at high temperature.

Although batch treatment may be the only viable option in certain circumstances many people have reservations about its efficiency. The key question is how persistent is the inhibitor film after it is laid down. Patches may be stripped off very quickly, perhaps by high velocity, and there is no way of knowing this unless one is fortunate enough to have monitoring probes at those precise locations. In continuous injection there is always a reservoir of dissolved inhibitor available to patch up stripped areas. In batch treatment these areas remain unprotected until the next batch is applied. And how frequent should the treatments be? Ideally, on-line monitoring should reveal when film breakdown starts and more inhibitor is needed. In practise it is logistics (e.g. the need to shut-in a well for a downhole treatment), economics (“how many treatments can we afford”) or limited lab data that often decide. Batch treatment is not fully understood and can not be used confidently as the only treatment method until the various uncertainties are removed.

The lab test for batch inhibitors is a rough but straightforward approximation of the full scale process. Steel specimens are dipped in the inhibitor, washed with distilled water to remove excess material, and then placed in the corrosion test cell or autoclave. The
corrosion rate is monitored against time for perhaps up to several months to see when breakdown occurs. A series of such tests enables the protection efficiencies and breakdown times of several different inhibitors to be compared (Figure 4). The washing step may be carried out with a hydrocarbon solvent instead of water. The intention is to remove any inhibitor which is simply adhering to the specimen via surface tension and is not actually associated with the surface film (this adhering material would be quickly washed off in the real system as well). The corrosion test is more realistic if dynamic fluid conditions are used (e.g. rotating annular cell, rotating cylinder electrode, recirculating flow loop...these are all described later).

Some Middle East operators take a fairly direct approach to selecting a corrosion inhibitor. They will simply ask a supplier for large quantities of a specific product based on its performance elsewhere even though the operating conditions may be completely different from their own installation. No further testing is carried out. This could well lead to problems. A product that works well in one environment may not do so in a different one so it is wise to check the inhibitor performance in a programme of lab tests.

The procedure used by BP in the UK North Sea is also followed by several other operators who do not have a service company alliance arrangement. A number of suppliers are invited to submit one or two

![Figure 4: Hypothetical Data from Static Persistency Tests on Batch Treatment Corrosion Inhibitors](image)

**Choosing a Corrosion Inhibitor for Continuous Treatment**

**General Outline**

Some Middle East operators take a fairly direct approach to selecting a corrosion inhibitor. They will simply ask a supplier for large quantities of a specific product based on its performance elsewhere even though the operating conditions may be completely different from their own installation. No further testing is carried out. This could well lead to problems. A product that works well in one environment may not do so in a different one so it is wise to check the inhibitor performance in a programme of lab tests.

The procedure used by BP in the UK North Sea is also followed by several other operators who do not have a service company alliance arrangement. A number of suppliers are invited to submit one or two
products for evaluation which is carried out either in-house or by a contractor laboratory. In the European Community there are fair trade regulations requiring that any contract worth >$280,000 over 4 years is openly advertised for tender. Therefore, any supplier who meets certain qualification criteria (e.g. British Standard or ISO accreditation) has a right to submit samples for consideration. The test programme will use a number of techniques - which are outlined below - to progressively narrow the shortlist down from ca 20 to ca 3 products. There can be subtle differences between labs in how the tests are carried out and interpreted. One lab may study dynamic conditions using a flow loop while another will use a rotating cylinder electrode. There are no standards in this area from a body such as the National Association of Corrosion Engineers. This situation is not ideal but ultimately it is the performance of the best lab products in field trials which will decide which product is finally selected.

Effective field performance is the over-riding objective. Laboratory testing is only ever an approximation of real conditions and while it will eliminate unsuitable products it can not guarantee to identify the best ones. Indeed, one North Sea platform apparently no longer bothers to carry out corrosion inhibitor pre-testing in the lab. The operator puts selected products straight into the field for testing. This is a high risk, trial and error strategy which relies entirely on effective field monitoring. Some preliminary testing is wise, if not in the lab then by a sidestream device in the field. Some inhibitor suppliers and corrosion consultancies have suitable sidestream equipment. Even here one must appreciate that the sidestream only approximates the true conditions. Flow regime, total pressure, and oil/water ratio are some of the variables that are likely to differ from those in the process line.

Before submitting a product, suppliers will normally carry out their own tests using conditions, and possibly fluids, supplied by the oil company. Existing products on the shelf will be examined first since it is a major task to start from scratch and formulate for a particular application (see Box 6), especially when there is no guarantee of any eventual revenue. This hardly limits the options available since many suppliers have hundreds of existing corrosion inhibitors in their range.
Many types of corrosion inhibitor test are used routinely for selection work in oil industry laboratories. The most sophisticated methods try to simulate field conditions as closely as possible by reproducing all aspects of composition, temperature, pressure and hydrodynamics. Other methods sacrifice some realism for speed and convenience. Ultimately, however, all tests are approximations of the full scale system. Slugging flow in multiphase flow lines and pipelines (i.e. gas + liquid) is an example of one particular case where realistic lab tests have not yet been fully developed or proven.

Figures 6 and 7 shows the steps currently followed by BP Sunbury to select the best corrosion inhibitor from a collection of products submitted by suppliers. This is a basic protocol and it would be altered accordingly to deal with specific demands or circumstances of any particular case. For example, in a high temperature situation (>100ºC) an autoclave would be used instead of a bubble test and an annular flow reactor instead of a flow loop. At each step along the arrow some products would be eliminated. Flow loop and

Box 6: Corrosion Inhibitor Composition

Oilfield CO₂ corrosion inhibitors typically contain from one to six organic components dissolved in a carrier solvent. The total solute fraction adds up to ca 30% w/w. The active components comprise mainly surface active (i.e. surfactant) type molecules such as alkyl amines, alkyl quaternary amines, alkylethoxyphosphates, imidazolines etc. Demulsifier species (e.g. ethoxylated phenol-formaldehyde resins) may also be included in order to reduce any impact on water/oil separation in the field. The carrier solvent can be water, alcohol or hydrocarbon. A low freezing point solvent (e.g. ethylene glycol) is required for products used in very cold conditions.

The efficient commercial products used today have evolved through much trial and error testing. Staff moves within the suppliers ensure that effective new ideas are eventually spread around since patents are not always issued or, if they are, can be difficult to enforce. However, there has been little real change in the basic chemistry used over the last 15 years. This may change with the current drive towards environmentally friendly products.

Detailed Selection Protocol

Many types of corrosion inhibitor test are used routinely for selection work in oil industry laboratories. The most sophisticated methods try to simulate field conditions as closely as possible by reproducing all aspects of composition, temperature, pressure and hydrodynamics. Other methods sacrifice some realism for speed and convenience. Ultimately, however, all tests are approximations of the full scale system. Slugging flow in multiphase flow lines and pipelines (i.e. gas + liquid) is an example of one particular case where realistic lab tests have not yet been fully developed or proven.

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**Figure 6 - BP Corrosion Inhibitor Selection Methods**

(a) Solubility Test
- corrosion inhibitors in water:
  - left: insoluble, not dispersible
  - right: dispersible

(b) Bubble Test

(c) Flow Loop

(d) Oil/Water Partitioning

(e) Rotating Cylinder Electrode

(f) High Pressure Flow Loop
partitioning tests are time consuming, and therefore a maximum of ca 6 products would be considered by that stage. Full details of all the techniques are already available [12]. Some outline notes are given opposite.

(a) decide test conditions - This is arguably the most important step: deciding how to simulate the field conditions and what compromises are possible, e.g.,

- use simulated brine instead of field brine. Field brine may not be available at all, may only be available with corrosion inhibitor already added, or may be unstable due to scaling.

- use carbon steel specimens throughout. This will not give specific information about weld corrosion. Making up representative weld specimens for corrosion testing is a difficult and expensive task though it can be addressed if necessary.

- use CO$_2$/N$_2$ mixtures to simulate the gas phase and so omit the natural gas components. The CO$_2$ partial pressure (i.e. pCO$_2$) is used to mimic field conditions. Normally pCO$_2$ < 1 bar and so a CO$_2$/N$_2$ mixture with 1 bar total pressure can be used. For a liquid stream in the field pressurised above its bubble point, the CO$_2$ partial pressure of the last gas phase in contact with the liquid is used, i.e. on the upstream side; the “virtual” partial pressure of CO$_2$ [13]. Alternatively, this value can be calculated using software such as the BP “SPARTAN” package.

- for a wet gas system use a simulated liquid phase by itself rather than the complete gas/liquid mixture.

- use wall shear stress to simulate hydrodynamics. There are many hydrodynamic variables which could be used (e.g. velocity, turbulent kinetic energy, Reynolds number, mass transfer co-efficient). Wall shear stress is appropriate to the region next to a metal surface and is especially relevant to the tendency to remove a corrosion inhibitor film. Box 7 shows equations for calculating wall shear stress in pipes.
**Figure 7: BP Corrosion Inhibitor Selection Strategy**

- **Decide Test Conditions**
  - **Solubility Test**
    - check dispersal in both oil and water
  - **Bubble Test**
    - rapid screening of all products under static conditions
  - **Flow Loop Test**
    - best products examined under dynamic conditions
  - **O/W Partitioning Test**
    - partitioning followed by flow loop to assess optimum field dosage on total fluids

- **Other Tests?**
  - **rotating cylinder electrode**
    - high shear (up to 80 Pa)
    - persistency tests
  - **compatibility tests**
    - does neat inhibitor attack metal?
    - does corrosion inhibitor interfere with demulsification or scale inhibition?
  - **jet impingement loop**
    - high shear (up to 300 Pa)
    - persistency tests
  - **high pressure loop**
    - for accurate simulation of real field conditions (3 days/test)

- **Recommend Products**
NACE Standard MR-01-75 defines a system as sour if the partial pressure of H$_2$S in the gas is >0.05 psi in a total pressure >65 psi. Materials selection to control sulphide stress cracking is then required. When selecting a corrosion inhibitor for a system containing both H$_2$S and CO$_2$ the BP Sunbury guideline is more qualitative. A useful rule of thumb is that CO$_2$ will produce three times as much aqueous corrosion as the same partial pressure of H$_2$S [16]. Therefore, when p CO$_2$ >> p H$_2$S most of the corrosion will be caused by CO$_2$. In these circumstances it is reasonable to omit the H$_2$S component in the corrosion tests. This is because at low concentrations H$_2$S can form FeS films on steel surfaces which can be protective. Reducing the baseline corrosion rate makes it more difficult or even impossible to discriminate between corrosion inhibitor candidates. Once an inhibitor has been selected in a CO$_2$-only system then H$_2$S can be included in final confirmation tests. However, it is worth remembering that some corrosion inhibitors are formulated to perform best on a complete or partial FeS film. These products

Box 7: Equation for Wall Shear Stress in a Pipe

The standard equation is derived from the work of Blasius [14, 15].

\[
\tau_p = 0.039 \rho u_p^2 \text{Re}^{-0.25}
\]

\( \tau \) is wall shear stress (Pa)
\( \rho \) is pipe
\( \text{Re} \) is the Reynolds number, \( \text{Re} = \frac{\rho ud}{\eta} \)
\( \rho \) is density (kg/m$^3$ ... 1000 for water)
\( u \) is velocity (m/s)
\( d \) is diameter (m)
\( \eta \) is viscosity (Pa s ... 0.001 for water)
\( u_p = \frac{4Q}{\pi d^2} \)
\( Q \) is pipe flow rate (m$^3$/s)

..therefore, \( \tau_p = 0.060 \rho^{0.75} Q^{1.75} d^{-3.75} \eta^{0.25} \)
are not likely to do well when H$_2$S is omitted from tests. A related point is that some corrosion inhibitors formulated for CO$_2$-only systems actually contain a sulphide component intended to enhance protection by deliberately forming FeS films.

When pCO$_2$ ~ pH$_2$S then H$_2$S must be included in the tests since it could be making a significant contribution to the overall corrosion. High H$_2$S situations are amongst the most difficult to inhibit, for example, in Canada where some wells produce >30% H$_2$S in the gas and require several hundred ppm of corrosion inhibitor [17]. High density polyethylene liners (HDPE) are often used instead.

After considering all these issues the main parameters required for the test programme are brine composition (including other oilfield chemicals, see “Compatibility Issues”, p.41), gas composition, temperature and wall shear stress. The tests should cover the expected variation in each parameter during the life of the field. Brine composition, for example, can change due to sea water breakthrough in the reservoir.

(b) solubility test - The wheel test is still often used as the first stage in selection. Weight loss coupons are added to many bottles containing a corrosion inhibitor in a test solution. The bottles are then sealed, mounted on the spokes of a wheel, and rotated to agitate the contents. This type of test is the only one which can be used at low water cuts (<5%) to evaluate oil soluble corrosion inhibitors. Nevertheless, random wetting effects can sometimes influence the trends observed. In contrast, the BP approach - bubble tests, flow loop tests and the others described below - concentrates on using a water phase and so water soluble inhibitors may arguably be favoured. This could cause problems because an entirely water soluble product is not suitable for deployment in a low water cut crude oil system: it would be difficult to deliver to all the water wet areas of the pipewalls.

To address this concern all products in the BP selection are first qualitatively checked for their solubility in brine and in crude oil (Figure 6(a)). A transparent oil such as “maltenes” (1:1:1 v/v xylene/kerosene/gas oil) is used to simulate crude oil [11]. Corrosion inhibitors must be soluble or dispersible in both brine and maltenes in order to proceed to the next stage of testing.
main tests - The bubble test, flow loop test and the others in Figure 6 are fully described elsewhere\textsuperscript{[12]}. Table 2 briefly summarises the main pros and cons of each method.

<table>
<thead>
<tr>
<th>Method</th>
<th>Pros</th>
<th>Cons</th>
<th>Maximum T (°C)</th>
<th>Maximum P (bar absolute)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bubble test</td>
<td>Convenient; many tests in short period; low liquid volume</td>
<td>Static</td>
<td>80</td>
<td>1</td>
</tr>
<tr>
<td>Autoclave</td>
<td>High T and P</td>
<td>Static; time consuming</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>Glass flow loop</td>
<td>Dynamic; &lt;7 Pa in 5 ltr loop; &lt;50 Pa in 16 ltr loop</td>
<td>Time consuming (1 day/test)</td>
<td>80</td>
<td>1</td>
</tr>
<tr>
<td>High pressure loop</td>
<td>Dynamic; high T and P</td>
<td>Time consuming (3 day/test)</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>Rotating cylinder electrode</td>
<td>Convenient; up to 80 Pa shear</td>
<td>Can underestimate corrosion compared to a flow loop and so is not as severe a test</td>
<td>80</td>
<td>1</td>
</tr>
<tr>
<td>Rotating annular cell</td>
<td>High T and P</td>
<td>Can underestimate corrosion compared to a flow loop and so is not as severe a test</td>
<td>120</td>
<td>30</td>
</tr>
<tr>
<td>Jet impingement loop</td>
<td>High shear (up to 300 Pa)</td>
<td>Can underestimate corrosion compared to a flow loop and so is not as severe a test</td>
<td>80</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 8 presents typical data from each stage of the testing showing how the best products are selected. In this hypothetical example six products are examined in the static bubble test (Figure 8(a)). Most give a satisfactory efficiency of >90% with respect to the baseline corrosion rate (ca 110 mpy) but two perform poorly (inhibitors A and B) and are eliminated. Two further products are eliminated under dynamic conditions in the flow loop (Figure 8(b)). The remaining inhibitors (E and F) are examined in more detail using water/oil partitioning tests. In each test a certain concentration of inhibitor is added to a
water/oil mixture, allowed to partition, then the water is separated and then transferred to the flow loop. Data for a range of concentrations reveals the optimum concentration (on total fluids) for a particular water cut, i.e. the onset of the plateau in Figure 8(c). Partitioning effects mean that this optimum concentration changes with changing water cut depending on the preferential solubility of the inhibitor. For example, going from 50 to 20% water cut reduces the inhibitor E efficiency but improves the inhibitor F efficiency (Figures 8(c) and (d)). This is because E is preferentially oil soluble and F is preferentially water soluble (Box 8). Overall, Figure 8 shows that F is the best product and it will give ca 95% inhibition efficiency when dosed at 15 ppm on total fluids into 20 - 50% water cuts.

**Figure 8:** Hypothetical Data from Corrosion Selection Tests
Note that BP Sunbury prefers to carry out partitioning in a dedicated vessel, separate the water, and then transfer the water to the test facility. This avoids the possibility of oil wetting effects obscuring the performance of aqueous corrosion inhibitor which is likely to happen if a 1:1 v/v brine/crude oil mixture is circulated round a flow loop. Since the use of a large dedicated vessel can be time-consuming, brine/crude oil mixtures are sometimes used directly in the bubble test if qualitative partitioning data is required quickly. Oil wetting of the probes can be avoided in the bubble test. Further details of the oil/water partitioning test are discussed in the next section.

Oil/Water Partitioning of Corrosion Inhibitor

All the suppliers and users whom we approached realised the importance of oil/water partitioning and accepted that it should be examined in any selection programme. Some commented that certain
corrosion inhibitors actually require oil in order to perform well. This particular feature can actually be tested simply by adding 500 ppm oil to the bubble or flow loop tests in Figure 7. It doesn't require a full partitioning test. Nevertheless, a partitioning test will have the same effect due to the dissolved and dispersed oil carried over in the separated water.

The main purpose of a partitioning test, however, is to estimate the inhibitor dose rate required on total fluids. A product may show good efficiency at 28 ppm in water only tests, but if it is added at 28 ppm to a 1:1 v/v water/oil mixture then most of the material may migrate into the oil perhaps giving concentrations of 37 ppm in the oil phase and only 18 ppm in the water (see Figure 9, Box 8). 18 ppm might not be sufficient to fully inhibit the water. In this example a dose rate of 56 ppm on total fluids would be required to give 28 ppm in the water phase. This illustrates the importance of conducting partitioning tests at realistic water/oil ratios, and also of adjusting injection rates with changing water cut.

Note that some operators specify a recommended inhibitor concentration in the water phase. They then use experimental data to work out the necessary concentration on total fluids for a given water cut.

**Box 8: Theory of Corrosion Inhibitor Partitioning Between Oil and Water Phases.**

The following information is only theory and must be used with care for any real situation.

**Partitioning Equations**

\[
\text{if } C_o V_o + C_w V_w = C_t \quad \text{and } C_w/C_o = P
\]

\[
\text{where } \begin{align*}
C & \text{ is concentration} \\
V & \text{ is volume fraction} \\
w & \text{ is water phase} \\
o & \text{ is oil phase} \\
t & \text{ is total fluids} \\
P & \text{ is partitioning co-efficient (water/oil))}
\end{align*}
\]

\[
\text{then } C_w = C_t \frac{P}{V_o + PV_w} \quad \text{and } C_o = C_t \frac{V_o}{V_o + PV_w}
\]

**Illustrations**

The Figures below show the partitioning behaviour for, (a) a preferentially water soluble component (P=2.0), and (b) a preferentially oil soluble component (P=0.5), added at 28 ppm on total fluids to a mixture containing 1:1 v/v oil/water.
The ideal partitioning behaviour for a corrosion inhibitor is relatively clear. A completely water soluble product will fully inhibit the aqueous phase if present at the optimum concentration. However, it will be difficult to disperse in a mainly oil and low water system. Depending on the formulation it could well plate out on the pipewall downstream of the injection point and not be delivered efficiently to water wet regions by the flowing liquid. Completely water soluble components are also said to form poor protective films anyway because they have little or no hydrophobic character. In contrast a completely oil soluble product will be well dispersed but will not inhibit the water. The best approach is to have a product with some affinity for both water and oil. In this way it can be dispersed in oil and also inhibit water once it encounters any. The ideal distribution between oil and water is still a matter of debate and will also depend on the application. Whatever characteristic is desired by a supplier it can be achieved by tailoring specific components (e.g. by lengthening a hydrocarbon chain to increase affinity for oil) or by mixing several components or solvents which have different properties.

These figures demonstrate some rules of thumb for a constant dose rate on total fluids;

- for a preferentially water soluble component the aqueous concentration will vary inversely with the water cut

- for a preferentially oil soluble component the aqueous concentration will vary directly with the water cut
The issue of components raises a problem over the use of “partition co-efficients” in the way they are defined in Box 8. Many corrosion inhibitors are a mixture of components, perhaps as many as six or more and each of these will have its own individual partition co-efficient dependent on the prevailing conditions. The “overall” partition co-efficient for the product will be a compound of the individual values and so will be even more dependant on conditions. Therefore, it is unwise to regard a partition co-efficient, obtained under one set of conditions, as a constant which can be extrapolated quantitatively to other conditions. Partitioning should be regarded as a more qualitative concept as in “preferentially water soluble” or “preferentially oil soluble” [18]. This advice is reinforced by the potential error in any measurement of partition co-efficient in the lab. Not only are there bulk oil and water phases but also oil/gas, oil/glass, water/glass and oil/water interfaces. Each of these may influence the perceived distribution across the oil and water. It is difficult to tell how much inhibitor may be retained in these interfaces because although the amount of inhibitor in the bulk water may be measurable, the amount in the bulk oil may be impossible to determine.

BP Sunbury avoid the technical problems of residual inhibitor analysis simply by measuring the corrosivity of the brine sample. The corrosion rate will be dependant on the mixture of components and the total amount of product which is present in the water phase. A calibration curve of corrosion rate versus corrosion inhibitor concentration in water can be used to relate the corrosion rate for any sample (e.g. water separated from a partitioning run) to the appropriate inhibitor concentration.
**Water Cut**

Any water cut can be examined in a partitioning test though for low water cuts the amount of brine available for separation and testing can become rather small. A 2% v/v water cut in a 20 ltr vessel means there is only 400 ml of brine. This is enough for a bubble test but not a flow loop test. Four repeats would be necessary to produce the 1.7 ltr needed for a flow loop test. BP’s largest lab partitioning vessel is currently 20 ltr which means that ca 15% is the lowest water cut which can be simulated in order to produce 1.7 ltr of brine for a flow loop test.

**Deciding Field Dose Rate**

The standard approach described by the suppliers and operators we interviewed was to determine an approximate dose rate from partitioning tests in the lab, start with this in the field, and then gradually reduce or increase the concentration to an optimum value using field monitoring. Typical concentrations are given in Box 9. Field monitoring must be effective and reliable before an operator can confidently justify a reduction in dose rate, especially by a large amount. The short term cost saving may not be worth the risk especially with a critical, high valve asset such as a sub-sea pipeline. The recent “Corrosion Monitoring Manual” [1] describes the techniques which can be used to manage gradual reductions in the dose rate.

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**Table 9: Typical Field Dose Rates for Corrosion Inhibitor**

The following data were gathered from suppliers and operators. The values are merely illustrations of typical dose rates for various cases and should not be used as definitive recommendations. Some examples of extreme situations are included.

<table>
<thead>
<tr>
<th>Location</th>
<th>Corrosion inhibitor dose on total fluids (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil well</td>
<td>50</td>
</tr>
<tr>
<td>Infield oil line</td>
<td>50</td>
</tr>
<tr>
<td>Short oil transport line</td>
<td>15</td>
</tr>
<tr>
<td>Long oil transport line</td>
<td>30</td>
</tr>
<tr>
<td>Long gas transport line</td>
<td>2 pint/MMSCF</td>
</tr>
</tbody>
</table>

**Extreme cases:**

- Hot, deep gas well: 2000
- 50% H₂S gas line: 1000
- High velocity, high water oil line: 250
Many interviewees felt that cutting the inhibitor dose rate was a “soft target” for cost savings and was often done carelessly because the repercussions were not always apparent until several years afterwards. Corrosion inhibitor can be described as a maintenance chemical rather than a process chemical. Operations can continue in the absence of inhibitor. However, degradation may eventually stop operations at some time in the future.

BPX Alaska are currently using a model which compares the whole life cost of corrosion inhibition plus associated monitoring against the risk and cost of line replacement [1]. This shows that high inhibitor dose rates maintain a low corrosion rate but are expensive in terms of chemical costs. Low inhibitor dose rates allow a high corrosion rate and are also expensive due to premature line replacement. There is an optimum dose rate between these extremes which gives the minimum whole life cost. At this concentration there is a small, non-zero corrosion rate and the chemical costs are balanced against the line replacement costs. The analysis shows that increasing the dose rate may sometimes be more cost effective overall than reducing the dose rate.

Even after a specific dose rate is decided it may still not be achieved in practise due to operational problems, errors or oversights. This issue is discussed in more detail under “Deployment” (p.49).

### Compatibility Issues

#### Metals
Strange as it may seem, some neat corrosion inhibitors can actually corrode metals [19]. They only perform as corrosion inhibitors when they are diluted to a small concentration in a process liquid. Because of this effect it is necessary to check the compatibility of neat corrosion inhibitor with the material used to fabricate the storage and delivery system. Simple coupon weight loss tests in aerated neat inhibitor are sufficient. 316 stainless steel understandably has a broader range of resistance than carbon steel and is the preferred material amongst several operators. The stainless steel injection quill must also be designed so as to avoid any neat inhibitor coming in contact with carbon steel pipe prior to mixing (see also Box 14). If a carbon steel pipe and quill is already in place then it may rule out the use of certain “corrosive” corrosion inhibitors. This must also be considered when batch treating a carbon steel line with neat or partially diluted (ca 20% v/v) corrosion inhibitor.

#### Lining Materials
Lined carbon steel storage vessels and delivery piping can be used as a compromise between stainless steel and carbon steel. Nevertheless,
lining materials themselves have their own limitations and can also be attacked by certain corrosion inhibitors. Compatibility tests are again necessary. The elastomer materials used as seals in pumpheads must also be considered. Viton A, for example, is vulnerable to the amines used in many corrosion inhibitors. There is a range of alternative materials (e.g. AFLAS, perfluoropolymers etc) which may be more effective (see Box 10). Unfortunately, with elastomer seals there is always a trade off between chemical resistance and useful mechanical properties.

Box 10: Seal Materials for Pumps

Although a rubber O-ring may only cost a few pounds, the cost and safety consequences of seal failure can be extremely large. It is, therefore, well worth giving detailed thought up-front to all the seals in inhibitor pump and control equipment, as well as in production and injection service. Just because most seals are “black and stretchy” does not necessarily mean that all O-rings will perform the same in any given oilfield service.

Many plastic and rubber materials are available for use as either primary or secondary pump seals. The ASTM abbreviations for some of the more common materials are:-

NBR - Nitrile elastomers  
FKM - “Viton”/“Fluorel” fluoroelastomers  
TFEP - Tetrafluoroethylene-propylene; “Aflas” fluoroelastomers  
FFKM - Perfluoroelastomers “Chemraz” and “Kalrez”  
PTFE - Polytetrafluoroethylene; “Teflon” is not an elastomer, but is chemically very resistant and can be made to seal by pressure or springs

Each of these materials has an envelope of conditions under which they show satisfactory long term sealing performance, and the user should refer to the “BPX Elastomer Selection Guidelines” for further details [20].

The process for the selection of seal material and geometry takes place through a logical consideration of the temperature, pressure and chemical environment of the sealing duty. These factors determine the requirements for not only the chemical resistance but also the mechanical properties of the seal. It is important to define the service conditions as completely as possible in order to select the most appropriate seal geometry and material.

The major chemical factors determining the effect of corrosion inhibitors on elastomers will be:

- Amine content, e.g. amines affect both nitriles and “Vitons”.
- Acidity/alkalinity, e.g. acids affect nitriles, alkalis affect “Vitons”.
- Solvent package, e.g. methanol swells “Viton A”, aromatics swell nitriles.

In general, pump seals see neat chemicals at relatively low temperature, while production seals see mostly dilute chemicals at somewhat higher temperature. If there is any doubt regarding the performance of a seal, testing should be carried out with particular inhibitors to demonstrate that the seal can function under the appropriate conditions.
Once a corrosion inhibitor is injected it must be compatible with the other oilfield chemicals present in the system such as demulsifiers, scale inhibitors, anti-foams, wax inhibitors etc, and vice-versa. To simplify the selection procedure the best approach is to decide which function has the highest priority (corrosion inhibition, scale inhibition, demulsification), choose the best chemical for that function, and then find compatible chemicals for the other functions. For example, if scale inhibition is the priority and a scale inhibitor has been selected then this should be included at an appropriate concentration in all the corrosion inhibitor selection tests (Figure 7). A number of suppliers said they were not always given correct details about other chemicals and this made it more difficult to submit effective products for consideration. They were “at the mercy of customers” in this respect. Generally, however, they felt that corrosion inhibitor performance tends to be robust towards other oilfield chemicals. On the other hand demulsifiers and scale inhibitors are often adversely affected by corrosion inhibitors. Because of this the corrosion inhibitor is added downstream of the water separation train in many installations.

Compatibility issues can become extremely complicated when fluids from different installations are co-mingled in shared pipeline facilities. The Forties main oil line is a good example. This already has ca 20 separate contributors although some of these are very small. A policy of uniform chemical usage in such systems will reduce the chances of compatibility problems. However, if the “standard” corrosion inhibitor is inefficient for any particular contributing stream then another will have to be used there after making sure that it won’t interfere with the “standard” inhibitor in the shared line. All contributors should have to notify the system operator well in advance of any potential changes in chemical type or dose rate (see also “Responsibilities”, p.61).

Incompatibilities between different chemicals can become all too evident when they mix in the same injection line, usually accidentally. Many suppliers gave examples of blockages caused by neat corrosion inhibitor going into a line previously used to dose wax inhibitor or scale inhibitor. Adequate flushing with a solvent or water is obviously necessary before changing a chemical in this way. Blockages are of particular concern in inaccessible umbilicals and flexibles leading to sub-sea wellheads because repairs can be difficult. Sometimes the blockage is not due to products mixing but to a carrier solvent (e.g. methanol) forming a viscous gel with the corrosion inhibitor or even dissolving some polymer tubing. All these examples reiterate the importance of checking the compatibility of the corrosion inhibitor with all materials it encounters.
**Combined Products**

One way of avoiding compatibility problems between different products is to use combined products. Combined scale and corrosion inhibitors are available from a number of suppliers. Many of these are simply mixtures of compatible, individual products although some multifunctional, single component products are being assessed. Combined products have the advantage of enabling one storage tank, one pump, and one injection line to be used for both scale and corrosion control. This is especially attractive for minimum facilities installations. On the negative side, there is some loss of flexibility in this approach. If the combined product is being dosed at a particular rate and then there is a sudden need to increase the concentration of scale inhibitor, this can only be done by also putting in more corrosion inhibitor which may not be needed. The product could be reformulated to meet the new balance between scale and corrosion inhibition (e.g. 2:1 v/v → 4:1 v/v scale inhibitor : corrosion inhibitor) but realistically this is likely to take a few weeks.

**Environmental Issues**

Environmental concerns are increasingly likely to influence the selection of oilfield production and drilling chemicals in all parts of the world. Currently there is no uniform, worldwide legislation and local regulations vary from place to place. The industry view is that North Sea activity is setting the trend in developing environmental legislation, particularly the Norwegian sector where there is already a CO₂ tax. At present each national sector in the North Sea requires its own specific criteria to be satisfied. However, all the governments are participating in a working group set up by the Paris Commission (PARCOM) to develop a common statutory testing and approval system for North Sea exploration and production chemicals. When that happens, the current voluntary notification scheme in the UK sector will become mandatory. The UK already has strict limits for onshore water disposal regulated by the National Rivers Authority. One operator felt that some NRA limits were already too strict.

**Future Legislation**

Until the PARCOM Working Group and other bodies around the world report their findings no-one is quite sure what sort of legislation will emerge. Suppliers and operators felt strongly that this was hindering the development of environmentally friendly oilfield chemicals. The environmental targets were either varied, moving or hidden. For example, it is not yet clear whether products which act and remain in a crude oil phase, like demulsifiers and anti-foams, even need to be especially environmentally friendly. They are present at ppm level in
crude oil which itself is comprised of potentially worse toxins (benzene, polyaromatics etc). Some suppliers have already made progress towards “green” corrosion inhibitors and most have a medium term aim to produce a complete range of green products.

This is certainly consistent with the demand from some North Sea operators. One said they “have a policy to use category 0 and 1 chemicals at all times” given acceptable performance and that “a green corrosion inhibitor would be preferred even if slightly less efficient than a competitor” (NB - 0 and 1 are the lowest ecotoxicological risk categories in current UK legislation). One supplier is already advertising a green corrosion inhibitor which is 60-70% biodegradable in 28 days and which performs as well as existing products. In all of this the issue of performance is key. It is no use having a green corrosion inhibitor for its own sake if it doesn’t do its job. As one operator put it, “a pipeline failure is very unfriendly to the environment”. Another operator said that the SFT, the Norwegian environmental authority, is prepared to accept usage of a conventional, more toxic product on performance grounds as long as greener products were included in the selection process and were shown to be inferior. The SFT has less stringent regulations on the corrosion inhibitor if the produced water is destined for re-injection.

Suppliers now have a challenge to develop green corrosion inhibitors which match or exceed the performance of conventional products. A more efficient product will mean a lower dose rate in the field which is another environmental benefit. There is a need to remove the occasional view that “if it’s green, it’s no good”. Some promising new chemistries have already been reported\textsuperscript{[21]}, including work on polyaspartates by BP\textsuperscript{[22]}. But more remains to be done. One barrier, though, to looking at completely novel chemistry is the European Inventory of Existing Commercial Chemical Substances (EINECS). Any chemical substance first marketed by the manufacturer or importer after 18 September 1981 must be notified to the national competent authority. Notification requires a dossier of information about the chemical covering identity, uses, quantities, disposal, physical properties, toxicology and ecotoxicological tests. It can cost up to ca $50,000 to register a new chemical for the first time. Oilfield chemical suppliers understandably prefer to avoid this large cost by only considering substances already on the list when they select possible components for corrosion inhibitor formulations and other products.
Overall, there is a trend towards environmentally friendly products but little definite legislation so far to enforce it. The trend is for evolution rather than revolution. One supplier even went as far to say that the oil companies “pay lip service to environmentalism” but in many regions are under little short term pressure to change their ways. Only when legislation is scheduled or announced are they likely to take significant action.

KEYPOINTS: Corrosion Inhibitor Selection

- Corrosion inhibitor squeezes into the reservoir are uncommon. As much as two-thirds of the inhibitor may be “lost” and, due to its surfactant nature, there can be reductions in well productivity.

- Batch treatment inhibition is not fully understood and can not be used confidently until various uncertainties are removed, in particular, doubts about the persistency of the inhibitor film after lay down. Continuous treatment is universally preferred amongst the oil and chemical companies we contacted.

- Batch treatment is only suitable when the application is non-severe, when continuous treatment is technically difficult (e.g. downhole in gas wells, remote locations) or when batch and continuous treatment are used together for severe or upset conditions.

- A batch or continuous inhibitor which performs well in one field may be inefficient in another under different conditions. Therefore, it is wise to check the performance beforehand in lab tests.
A full corrosion inhibitor selection programme in the laboratory is an efficient way to choose a product. However, laboratory testing is only ever an approximation of real conditions and so it gives approximately the best products. These must then be further assessed in the field.

The BP selection strategy for continuous corrosion inhibitors has evolved over more than ten years. A shortlist of products is narrowed down through a series of solubility tests, static and dynamic corrosion tests, and water/oil partitioning runs.

The main purpose of a partitioning test is to estimate the inhibitor dose rate required on total fluids. For example, a product may show good efficiency at 25 ppm in water-only tests, but 60 ppm may be needed in a water/oil mixture in order to reach the same efficiency.

Due to the many components in proprietary corrosion inhibitor packages and also measurement artefacts, partitioning should be regarded as a qualitative concept - as in “preferentially water soluble” or “preferentially oil soluble” - rather than a numerical constant to be used for extrapolating to different conditions.

The dose rate determined in the lab should be introduced in the field and then gradually reduced or increased to an optimum value using field monitoring. However, cutting the operational dose rate is sometimes regarded as a soft target for cost savings. It should be done carefully in order to avoid undesirable repercussions.

Field corrosion monitoring must be effective and reliable before an operator can confidently justify a reduction in dose rate, especially by a large amount.

It is essential to check the compatibility of a corrosion inhibitor with every material, lining, seal, and oilfield chemical with which it is likely to come in contact. Incompatibilities of any sort can cause serious operational problems.

Environmental concerns are increasingly likely to influence the selection of all types of oilfield chemicals. To date there has been some evolution towards environmentally friendly corrosion inhibitors but not yet any definite legislation to enforce it or recommendations to guide it.
Oil company/chemical company alliances are starting up around the world as a new way of organising the selection and deployment of oilfield chemicals. The details of each arrangement vary enormously from a virtual sub-contracting of all aspects of chemical usage to simply a closer working relationship. All the alliance partners to whom we spoke stressed the careful planning necessary to define specific targets and roles. It is not yet clear if this alignment of operators with one particular supplier is just a fashion or is a long term trend. The arrangements themselves are really still on trial.

The points below summarise industry arguments we noted for and against the general concept of alliances, with particular regard to corrosion inhibitor deployment. Firstly, the main arguments in favour,

- **more streamlined logistics** - some suppliers regard the traditional relationship with operators as like a “one way mirror”, handing over samples and information and receiving little or no feedback. In an alliance the two can work together towards a common performance target, “rowing the boat together”, and bringing more resources to bear on a problem.

- **cost savings** - Instead of the operator buying just a corrosion inhibitor from a supplier they buy an “agreed corrosion rate” and both sides can share the cost benefit arising from a possible reduction in dosage levels. There might also be scope to share R&D spending.

One operator emphasised that alliances were a new way of thinking and working, and that “fear” was preventing some companies pursuing the idea. They further stressed that in order to be effective the concept had to be grasped company-wide and should not simply be adopted piecemeal by individual operating units.

Here are the main arguments against,

- **operator bears all risk** - Although the supplier may be closely involved in day-to-day deployment of corrosion inhibitor it is the operator who bears all the risk for liability and replacement costs in the event of a failure. Because of this, some say that the operator should take direct responsibility for inhibitor
deployment and not work through a contractor. The opposing view is that the operator will always be supervising the performance targets and the supplier is motivated by the risk of losing a contract.

- **supplier no longer competing** - Once in an alliance a supplier is no longer actively competing with other companies for business with the particular operator. There is a chance that complacency may creep in. After a few years it may become very difficult to change suppliers, if the need arises, because by then they will have become well integrated into operations and also hold a lot of important expertise and experience.

- **other suppliers stop co-operating** - The alliance supplier would prefer to use all its own products wherever possible but it can not always match the performance of the incumbent chemicals, so it may need to retain some of these. One problem so far has been that the alliance supplier sometimes has problems purchasing a product from another supplier either because of technical or commercial confidentiality or just plain envy. One solution is for the oil company to purchase from the other supplier. Oilfield chemical alliances are in their infancy and the industry is still developing appropriate working practises.

- **lose small suppliers** - If alliances become the norm there is a danger that only the large suppliers will survive. The smaller companies, perhaps specialising in niche products, may not be able to compete. If they disappear there may be less innovation and certainly less choice.

- **operator dictates supplier profits** - Some suppliers speculate whether alliances are really a way for operators to cynically squeeze prices by demanding a detailed knowledge of supplier costs using “open book” policies.

This section is only a summary of the main industry views. It does not seek to make an overall judgement about alliances. However, it is worth remembering that alliance or contracting relationships already exist in many important oilfield areas such as fabrication, drilling, supply etc. It is no surprise that such arrangements are being introduced more widely given the reorganisations and the focus on performance which have taken place in most oil companies over the last few years.
Quality Control of Corrosion Inhibitor Supplies

The majority of manufacturers of production chemicals apply strict QA/QC at all stages of processing, from receipt of raw materials to supply offshore. There is, therefore, an auditable quality trail throughout manufacture and supply. The use of the various quality standards such as BS 5750 and ISO 9000, although burdening in terms of paper work, ensure best practise and assure product quality (Box 12). Chemical manufacturers will provide a certificate of analysis (COE) if requested. Many methods are used for QC during manufacture and for final product analysis. Techniques employed may range from colour and amine number determination through to more sophisticated chemical analysis techniques such as HPLC, GPC, FTIR, ICP, MS, and NMR (see Box 13). Essentially the customers can have whatever QC and documentation they require.

Box 12: ISO Quality Standards
Customer expectations drive the basic requirements for the quality of any product or service. Moreover, continual improvements in quality are usually needed to improve or even sustain good economic performance. In this respect, the organisational system which produces a product or service is as important as the technical specification to which it is produced. In order to manage this aspect of quality, an extensive set of international quality system standards is now available and widely used.

The series of ISO standards - 9000 through 9004 - bring together and rationalise many of the individual national approaches to quality. ISO 9000 is a general overview and ISO 9001 - 9004 refer to specific aspects of providing a product or service to a customer. For example, ISO 9001 covers design/development and manufacturing while ISO 9002 covers production and installation. Quality systems essentially complement the requirements laid out in technical specifications, and provide the supplier and customer with an auditable trail of documented quality measures and checks. Most oilfield chemical suppliers are now accredited to ISO 9000 or equivalent.

Box 13: Some Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>QA</td>
<td>quality assurance</td>
</tr>
<tr>
<td>QC</td>
<td>quality control</td>
</tr>
<tr>
<td>HPLC</td>
<td>high pressure liquid chromatography</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infra-red spectroscopy</td>
</tr>
<tr>
<td>ICP</td>
<td>inductively coupled plasma emission spectroscopy</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectroscopy</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>ISO</td>
<td>International Standards Organisation</td>
</tr>
</tbody>
</table>
The approach of operators to quality is rather more variable. In terms of frequency and complexity of independent analysis, it often depends on previous experience, with major past problems often leading to major current effort in QA. Several operators rely solely on quality standard accreditation of pre-qualified and audited service companies. The degree to which regular auditing occurs after this qualification is very variable. By contrast, other operators insist on analysing samples taken from every tanker, pod or drum which they receive, and several companies have developed complex analytical routines for the QA of chemical supplies. The tendency to use this extreme approach is lessening, however, due to the increased influence and success of quality standards and the reasonable view that supplier partners merit some trust. Several operators adopt a compromise between these extremes by making brief checks on occasional random samples.

The QA/QC of chemical supplies essentially guarantees chemical composition but says little about chemical performance. A sensible approach is, therefore, to closely monitor the field performance of chemicals and to trace back along the quality audit trail if there are any performance problems or doubts which require further investigation. In the case of corrosion inhibitors, a performance test on every batch using a laboratory bubble test (Figure 6(b)) is a simple and useful precautionary measure which can easily be carried out by suppliers. Not many do this at the moment.

**Corrosion Inhibitor Pumping Problems**

Operators and suppliers have encountered many problems simply trying to pump corrosion inhibitor into a system. A number of these are obvious in hindsight. Suppliers commented that when they are called onto a site to examine a corrosion problem the first question they ask is, “...is the corrosion inhibitor going in?”. Frequently it is not. Good procedures and training are required to ensure that the inhibitor is effectively delivered to where it is needed.

The following list divides the various pumping problems between those relating to the inhibitor and those relating to the pump. Firstly, those relating to the corrosion inhibitor,

- **inhibitor viscosity** - The viscosity of any chemical will rise when it is cooled in sub-sea umbilicals, or when it is used in...
cold climates. Viscosity measurements should be carried out at
temperatures appropriate to how and where the inhibitor is to
be used.

- compatibility of inhibitor with pump materials - The
  compatibility of neat inhibitor with metals has already been
  covered in detail (p.41). The inhibitor must also be compatible
  with the pump seals (Box 10, p.42).

- line blockages - Due to poor cleaning when chemicals are
  changed over.

- inhibitor storage tank empty - The storage tank must be
  regularly checked to ensure timely reordering of inhibitor
  supplies. One should avoid getting into a situation where the
dose rate must be halved in order to conserve stocks until the
next supply arrives.

- abrasive particles in inhibitor - If fine solids such as blasting
  sand find their way into the inhibitor storage tank they can
  abrade pump seals and cause leaks.

Secondly, here are problems relating to the pump and other
hardware,

- wrong dose rate - This can happen if the pump is not
  calibrated, or is improperly controlled. If certain valves are
  closed then the dose rate may be zero. Errors are also possible
  when using tank level readings or calibration cylinders at the
  pump suction in order to calculate the dose rate.

- pump wrongly sized - This can make it difficult to dose at the
  recommended rate. It may be necessary to reformulate the
corrosion inhibitor - either diluting or concentrating the active
components - in order to accommodate the available pumping
capacity. Incorrect sizing may be a particular problem when the
dose rate has to be changed frequently to match variations in
process conditions (e.g. changing water cut).

- air locks - Certain types of pump appear to be prone to air
  locks.

- poor delivery system design/installation - One pump may be
delivering into several lines or wellheads all at different pressures.
The high pressure lines may not receive any inhibitor. Such manifoldeed delivery systems are more difficult to check than dedicated pumps unless special “Sko-Flo” valves are used. These maintain a constant flow rate despite varying differential pressure. In another example an operator described how the inhibitor delivery line was inadvertently routed into the platform drain rather than the process, an extreme example of poor installation.

- **dosing downhole** - Injection can be particularly troublesome downhole (see p.23). Injection via the lift gas may lead to gunking as the solvents evaporate, and chemical injection valves operating on annulus pressure may actually dose batch-wise rather than continuously.

In summary, it is clear that many pump problems are avoidable if the pumps are designed, maintained and operated correctly. It is important to have written procedures covering calibration, operation and maintenance. Operating and supervisory personnel alike need to be made aware of the importance of dosing on a regular day-to-day basis.

### Injecting Inhibitor Into The Process Stream

#### Injection Location

The industry rule of thumb is to inject the corrosion inhibitor as far upstream as possible. This will enable the inhibitor to reach all vulnerable areas. In practise, downhole injection is difficult and prone to problems (see p.23). Therefore, the inhibitor can be added at the wellhead. However, it is more appropriate to inject immediately downstream of the final stage oil/water separator if the separation process might be upset by corrosion inhibitor, if large amounts of corrosion inhibitor are likely to be lost with the separator water, and if the corrosion inhibitor is primarily intended to protect an export pipeline rather than the processing equipment.

Many operators do not use corrosion inhibitor to protect process equipment. This is either because corrosion resistant alloys are prevalent or because uninhibited carbon steel sections are regularly checked and replaced when necessary. Furthermore, it can be difficult to deliver inhibitor effectively into stagnant bypass or drain line piping. Inhibitor might only be added upstream of an area which prediction or experience has shown to be at high risk, e.g. high velocity bends, tees.

All of this discussion describes the optimum situation, which is reliant on good corrosion engineering design. Many production sites have to
make do with the injection points that are in place and which may not be ideal. Retrofitting a new injection point might be necessary if a particular corrosion problem gets out of control.

Whatever injection points are used it is important that the inhibitor is well mixed into the liquid or gas stream. This is achieved by injecting just upstream of a turbulent region (e.g. bend, valve, pump) or directly into a turbulent process stream. The mixing length will be a function of the process conditions (e.g. Reynolds number, pipe diameter etc) but for true turbulent flow is likely to be less than ten pipe diameters (this mixing length is actually CRA construction in a few installations). In contrast, the inhibitor may never thoroughly mix in laminar flow. An atomising injection quill or creation of turbulence using a valve may be required in this case. Details of the types of injection tube available, and the optimum position of the tube in the pipe are given in Box 14. Details on whether the inhibitor should be used as-received or diluted in a solvent are given in Box 15.

**Box 14: Injection Tubes for Pipelines**

It is important to use correctly positioned injection tubes in order to disperse the corrosion inhibitor and also to prevent the neat product contacting the pipewall (see Figure 11) because some neat corrosion inhibitors can corrode the pipewall (see p.41). The injection tube itself must also be resistant to the neat inhibitor. Tubes with diagonally slanted tips, i.e. quills, are widely used \[23\]. Typically, the quill tip should have a 45° spray and be located midstream, facing back into the direction of flow. However, one operator said they “had looked at all sorts of configurations and it made no difference”.

If pigging is to be performed in the line, then a tube which is retractable or which is flush to the pipewall is required. A mark or scale on the side of the tube helps to ensure correct positioning; quills have sometimes been pushed so far into a pipe that they contact the opposite wall. Local turbulence will always improve the dispersion efficiency and it is particularly necessary for flush injection. In a laminar or stratified flow system the quill tip should be placed directly in the water phase.

Atomising quills can be used to achieve good dispersion in gas systems or laminar liquid systems. The higher the differential pressure across the tip then the smaller the dispersed droplets. Typical quills for liquid and gas streams have a quarter inch internal diameter. However, in some gas systems where the inhibitor is diluted into a large volume of methanol or glycol (i.e. hydrate inhibitor) before injection then a larger delivery tube is necessary and the injection point becomes more like a “tee”.

**Figure 11: Injection Quills**
After choosing carbon steel and corrosion inhibitor for a process system, selecting the inhibitor, and finally deploying it, the crucial question is, “does it work?”. Corrosion monitoring should be able to provide the answer. Monitoring is such an important area that it is covered in detail by a companion set of guidelines [1]. As with other aspects of corrosion control, care and attention to detail are required in order to obtain meaningful results.

**Box 15: Dilution of Corrosion Inhibitor in the Field**

- Oil pipelines are normally dosed with as-received corrosion inhibitors.
- Gas lines employ inhibitor diluted in methanol, or some other alcohol based hydrate inhibitor/suppressant. Concentrations typically range from 0.5% up to 5 or 10% in methanol when hydrate treatment is required. It should be remembered that many corrosion inhibitors are only marginally soluble in methanol at low temperature. Dry gas lines, where the product is dewpoint adjusted and TEG dried, will not normally be inhibited.
- Downhole injection typically employs 1% - 20% corrosion inhibitor diluted in crude oil or diesel. The dilution reduces the total amount of corrosion inhibitor which is stored in the annulus.
- Batch chemicals are diluted in a locally available solvent, as large volumes are needed. The diluent will typically be crude oil, condensate, diesel or deaerated seawater, with 1:4 v/v inhibitor/diluent between pigs for pipelines.
- Whenever inhibitors are employed in diluted form there must be adequate control over the quality of the diluent used and proper supervision of the dilution process.
- More generally, inhibitors may also be concentrated for international business to save on transportation costs or to introduce local labour and materials into a product.

**Corrosion Monitoring**

After choosing carbon steel and corrosion inhibitor for a process system, selecting the inhibitor, and finally deploying it, the crucial question is, “does it work?”. Corrosion monitoring should be able to provide the answer. Monitoring is such an important area that it is covered in detail by a companion set of guidelines [1]. As with other aspects of corrosion control, care and attention to detail are required in order to obtain meaningful results.

**Dealing with Process Changes**

**Managing Corrosion**

It is essential to actively manage corrosion inhibition. Once an inhibitor is selected and deployed an operator shouldn’t just forget about it and think that “no news is good news”. This policy, or really lack of policy, has led to significant problems in the past. Furthermore, the responsibilities of everyone involved in corrosion
control must be well defined in order to manage effectively. Organisations where “everyone has a dabble” are likely to have problems such as the case of a Middle Eastern operator who had to put a lock on the corrosion inhibitor delivery pump to prevent unauthorised changes in the dose rate. When there is no strategy or a badly defined strategy then the response to a corrosion problem is likely to be slow at best and non-existent at worst. Several operators quoted a slow initial response as the primary cause of some of their most serious corrosion problems. Therefore, a well thought out corrosion management strategy (CMS) which includes clearly defined roles and responsibilities is recommended for all BPX sites in order to assign the day-to-day responsibilities for confirming effective performance, and to specifying responses to the common process changes.

Certain types of corrosion monitoring (e.g. weight loss coupons) only reveal an adverse change in the process after it has happened. These warnings are retrospective and metal loss has already occurred. It is obviously more efficient to pick up the process change as quickly as possible and respond to it immediately. Methods such as LPR (Linear Polarisation Resistance), which give an instantaneous measure of the corrosion rate, can be used for this but only if the conditions are suitable (water cut >ca 40% v/v required for accurate LPR). An alternative, or complementary approach is to continuously monitor a number of process parameters (e.g. flow rate, water cut, temperature etc) and be ready to alter the corrosion inhibition conditions appropriately. In BPX Alaska the production rates, pCO₂ and quantity of sand in multiphase flow lines are put into a flow model to calculate the optimum corrosion inhibitor dose rate and the necessary inspection frequency. These process data can later be correlated with corrosion monitoring information in order to check whether corrosion was adequately controlled.

Corrosion inhibitor dose rate is clearly a crucial parameter (see p.41) and should be checked daily. This apparently simple task is nevertheless prone to error. One operator described a case where its staff were reading the pump sight glasses incorrectly and so were putting in a much lower dose rate than planned. Sometimes it is the supply company who first notices this type of mistake because they eventually see that the quantity of inhibitor ordered over a certain period is not consistent with the stated dose rate. Figure 12 shows an actual field record from a site where the target inhibitor concentration of 50 ppm was rarely achieved over a 18 month period.
Table 4 (p.60) lists the main process parameters which affect corrosion and which should be measured and acted on whenever they change. Corrosion inhibitor type and concentration are the two controlling variables accessible to an operator. The inhibitor delivery rate is usually matched to the maximum throughput in the process (No.1, Table 4) so as to give the desired concentration on total fluids. If the throughput goes down for a day or so then the inhibitor delivery may not be adjusted and the prevailing concentration will therefore rise. However, if the throughput goes up then the inhibitor delivery rate must also go up to compensate. It may even be necessary to reselect the inhibitor if it cannot cope with a substantially higher wall shear stress.

Water cut is a key parameter (No.2, Table 4). It affects how the inhibitor partitions between oil and water phases. This is described in detail on p.36. The response to a water cut change depends on whether the inhibitor is preferentially oil or water soluble. When the water cut increases then the concentration on total fluids of a preferentially water soluble inhibitor must also increase in order to maintain the same concentration in the water phase (Figure 9). Another way of saying this is that the concentration with respect to the water phase must remain constant.

These implications of partitioning are widely understood amongst suppliers and operators. Most operators have a policy for changing the inhibitor concentration on total fluids depending on the water cut (e.g. 10 ppm for <5% water, 20 ppm for 5-10% water, 30 ppm for >10% water). Ideally this link could be automated but this would only be feasible if the water cut was continuously monitored. Most operators only measure it a couple of times per day. This of course
means that changing water cuts may pass through the system without corrosion inhibitor adjustment until the next water cut measurement is made. More frequent water measurements are advisable if water slugging is prevalent. Sometimes periods of high water cut are entirely predictable such as when an export line is used as a drain because of problems with produced water treatment plant. The corrosion inhibitor concentration on total fluids should be adjusted accordingly.

Regular pigging of pipelines to remove the water accumulated in low spots will help to minimise corrosion. This is because even if the water starts off as fully inhibited it is possible for the inhibitor to gradually degrade in a stagnant pool and to become ineffective. For pipelines with very low water cuts (eg < ca 0.05%) an elastomer cup type pig applied once a month is likely to be sufficient. Higher water cuts will require more frequent pigging, perhaps as often as once every few days.

Removal of the stagnant water by pigging will also help to reduce microbiological activity in the pipeline. It will minimise the chances of corrosive colonies becoming established on the pipewall and causing microbiologically induced corrosion (MIC). Some operators take the extra precaution of batch dosing with a biocide every month. In BP, however, most operators have tended to rely on regular pigging and also the biostatic action of certain continuous corrosion inhibitors in order to minimise any MIC.

**Aqueous pH**

The liquid pH (No.6, Table 4) is difficult to measure on-line and is sometimes calculated from the brine composition and pCO$_2$ instead. When sea water breakthrough occurs in a reservoir the overall salinity and buffering capacity (i.e. [NaHCO$_3$]) of the produced water will change possibly for the worse. One operator described how sea water breakthrough caused the pH to decrease and the corrosion rate to rise from 0.5 to 6.0 mm/year.

**Free Oxygen**

Free oxygen is not normally encountered in oil and gas production streams (No.5, Table 4). Any oxygen originally present in the reservoir will have been consumed in oxidation reactions with the hydrocarbons during the millions of years of storage at high temperature and pressure. However, free oxygen can enter the production process inadvertently and then cause corrosion problems because the corrosion inhibitors selected for CO$_2$ and H$_2$S environments may not be effective against O$_2$ corrosion. It may be necessary to reselect or augment the original inhibitor. A case where aerated sump oil was injected back into the process train is one example of oxygen ingress.
**TABLE 4: Some Process Parameters Which Can Affect Corrosion Rate**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Change</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Flow rates (oil/water/gas)</td>
<td>+ or -</td>
<td>Alter CI delivery rate to maintain concentration in water</td>
</tr>
<tr>
<td>2. Water cut</td>
<td>+ or -</td>
<td>May increase or decrease CI delivery depending on its o/w partitioning properties</td>
</tr>
<tr>
<td>3. Temperature</td>
<td>+</td>
<td>Increase [CI]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Scope to reduce [CI]</td>
</tr>
<tr>
<td>4. pCO₂ and pH₂S in gas</td>
<td>+</td>
<td>Increase [CI]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Scope to reduce [CI]</td>
</tr>
<tr>
<td>5. pO₂ in gas</td>
<td>+</td>
<td>May need to reselect CI</td>
</tr>
<tr>
<td>6. pH</td>
<td>+</td>
<td>Scope to reduce [CI]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Increase [CI], may need to reselect</td>
</tr>
<tr>
<td>7. Sand</td>
<td>+</td>
<td>Reselect CI and/or increase [CI], reduce velocity, install downhole sand screen</td>
</tr>
</tbody>
</table>

Notes: + ...increase
- ...decrease
pCO₂ ...partial pressure of CO₂

**Dealing with Process Interruptions**

This is not intended to be an exhaustive list of interruptions. There are likely to be other possibilities. Industry views on interruptions and changes varied from “not that frequent” to “probably happens more often than you think and normally goes unnoticed”. After any severe interruption or upset it may be necessary to apply a batch treatment before resuming continuous inhibitor injection.

**Shutdowns**

When shutting down a process line it is wise to shut-off the corrosion inhibitor delivery at the same time. Otherwise, neat inhibitor will be injected into a region of static fluid and quickly build up the
concentration to possibly corrosive levels. If a shut-in line is subsequently filled with water for inspection purposes then this water must be fully deaerated and inhibited. Care is also necessary when restarting the line because, in some facilities, the pipelines must be restarted before the water treating equipment. This means that high water cuts can go down the pipe until the water treatment begins. Extra corrosion inhibitor may be needed.

Acid stimulation of producing reservoirs and acid descaling of production tubing have gained notorious reputations for causing corrosion problems, though in some cases they may simply be convenient scapegoats for shortcomings elsewhere. The BPX Forties asset has developed a neutralisation procedure for acid returns using caustic soda solution (NaOH) which will substantially reduce the brine corrosivity should any of it enter the production stream. Initial fluid returns from scale squeezes may also be slightly acidic because many scale inhibitors are derivatives of weak phosphorus based acids. However, the real problem with scale squeeze returns is that they may be incompatible with the corrosion inhibitor. Compatibility should be checked before deployment.

Responsibilities

With the advent of the various types of alliance there is now a wide range of organisational structures for selecting and deploying corrosion inhibitors in oil and gas fields. Whatever approach is chosen it is important to define responsibilities as closely as possible through a Corrosion Management Strategy (CMS) or an Alliance Agreement. Many corrosion problems occur through complacency which often arises because the consequences of action, or inaction, may not be apparent for several years. It may be a cliché but it’s nevertheless true that effective corrosion control requires genuine commitment to the management strategy by all parties. This includes operational staff who are in control of many routine but nonetheless critical aspects of inhibitor deployment. Some awareness training may be necessary to ensure that these personnel view inhibitor issues with enough priority and interest. This will be helped by simple measures such as making staff aware of the results of sampling and measurements they have taken, and thereby showing how their actions (care or lack of care) can influence important decisions. Overall, the CMS should describe how process, dosing, monitoring and inspection data are brought together and analysed. Complete and continuous records are necessary to enable this.
Sharing information and learning from mistakes and near misses is also important. Networks can work well within operating companies, e.g. between production chemists, corrosion engineers etc. However, industry cutbacks now mean that fewer people have the time to organise them. Real effort is needed to ensure that individual assets can learn from each other’s mistakes and experiences. On an industry wide level there is no specific, formal mechanism for sharing corrosion inhibitor experience. Successful applications may be discussed at relevant conferences and meetings, but the open discussion of problems and failures is generally more problematic. Despite the fact that time and money can be saved via dialogue, there is often only frank exchange of views and experience if there is a common short term interest.

**KEYPOINTS : Deployment**

- Alliances or contracting relationships already exist in many important oilfield areas so it is no surprise that such arrangements are now being introduced more widely for the selection and deployment of oilfield chemicals. There are potential advantages and disadvantages in this trend.

- Only those suppliers meeting a recognised quality standard such as ISO9000 should be used. A simple performance test on every batch of corrosion inhibitor is a useful precaution easily accommodated by suppliers.

- Pump problems can be due to both poor design and poor operation. Many of the operational problems (e.g. bad calibration, inhibitor supply exhausted) can be avoided through good procedures and training.

- The corrosion inhibitor should be injected as far upstream as possible. This often means at the wellhead in order to protect process equipment already known or predicted to give a corrosion problem (possibly certain bends or tees).

- Injection immediately downstream of the final stage oil/water separator is appropriate if the separation process might be upset by corrosion inhibitor, if large amounts of corrosion inhibitor are likely to be lost with the separated water, and if the corrosion inhibitor is primarily intended to protect an export pipeline rather than the processing equipment.
The inhibitor must be added just upstream of a turbulent region (e.g. bend, valve, pump) or directly into a turbulent process stream to ensure good mixing.

Typically the injection quill should be positioned midstream, facing against the flow (unless pigging requirements prevent it). Direct injection into any water phase is needed for laminar or stratified flow conditions.

Corrosion inhibitor is often diluted in solvent for use in gas lines, downhole injection, and batch treatment. There must be adequate control over both the diluent and the dilution process.

Field corrosion monitoring is covered in detail in a companion document.

An immediate response to certain key process changes will reduce the corrosion risk. The inhibitor type and dose rate should be continuously matched to the process throughput, water cut, CO₂ level, O₂ level, H₂S level, pH and sand production.

Process interruptions like shutdowns and acid returns require their own special set of precautions to prevent corrosion damage.

It is essential to actively manage corrosion using a Corrosion Management Strategy with all parties having clearly understood accountabilities.

Sharing information about corrosion experiences and near misses, both within BP and externally, often repays the effort required.


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Index

A
acid 61
alliances 49 - 50

B
biocide 18 - 19, 59
BS 5750 51

carbon steel 13 - 14
cladding 12
corrosion
design 15 - 16
effect of process variables 60
management 56, 61 - 62
microbiologically induced. 59
monitoring 15, 56, 57
prediction 15
corrosion inhibitor
batch treatment 23 - 26
compatibility 33, 41 - 44
composition 28, 44
continuous treatment 24 - 27
dilution 56
field dose rate 40, 57 - 58
injection 16, 43, 54 - 56
mechanism 24
metal surface area and. 16
mixing 55
partitioning in oil and water 36 - 40
residual analysis 39
selection 25 - 46
solubility 33
squeeze treatment 23
vapour phase inhibitors 18
viscosity 52
when to start injecting 19 - 20
INDEX

corrosion inhibitor tests
  batch treatment 25 - 26
  conditions in. 30 - 33
  continuous treatment 25 - 46
  H₂S and. 32
  limitations 27
  list of. 29, 34
corrosion resistant alloy (CRA) 11 - 13

E
environmental issues 19, 44 - 46

G
gas buffering 14
gas pipelines 14

H
hydrostatic testing 17 - 20

I
interruptions 60 - 61
ISO 9000 51

N
non-metallic materials 12

O
oxygen 18, 19, 59, 61
oxygen scavenger 18

P
pigging 14, 59
pitting corrosion 13
pumps
  problems 52 - 54
  seals 42

Q
quality control 51 - 52
quills 55
S
scale squeeze 61
shared pipelines 43
stress corrosion cracking (SCC) 13

T
13% Cr steel 11

W
wall shear stress 30, 32
water cut 58 - 59
welds 13, 16, 30
whole life costing 13