Control of corrosion in oil and gas production tubing

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Controlling corrosion in production tubing is essential for maintaining production and for preventing loss of well control. Materials for use downhole have to meet criteria for corrosion resistance and also mechanical requirements. The potential corrosion rate can be estimated and the risks of sulphide stress corrosion cracking assessed on the basis of the anticipated environmental conditions and flow regime. Material options for tubing can then be considered on the basis of published corrosion test data and also field experience. Candidate materials may be tested under the precise field conditions expected in order to ensure that overconservative choices are not made. Corrosion inhibitors, coated carbon steel, and fibre reinforced plastic tubing have temperature, flow regime, and mechanical limitations. Specific corrosion resistant alloys (CRAs) have environmental limitations with respect to temperature, hydrogen sulphide, and chloride content. Details of field experience with all of these material options are given. There exists a large amount of experience with CRAs for downhole applications. Correctly selected CRAs have a good track record of service, even for hostile, H₂S containing conditions. There are a few limited examples of CRA clad tubing. This product may be one that needs re-evaluation as it offers potential for economic use of costly but effective CRAs.

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INTRODUCTION

Production tubing is the conduit through which fluids are transported from the reservoir to the surface facilities. The tubing has to withstand corrosion from any aqueous phase produced with hydrocarbons and containing dissolved acid gases (e.g. CO₂ and H₂S) and salts (e.g. chloride ions). Corrosion control is essential for maintaining production and avoiding the risk of loss of well control.

Materials for use downhole have to meet criteria for corrosion resistance and also mechanical requirements. It is possible to establish a logical series of steps for material selection, incorporating analyses of the environment, corrosion rate calculations, and final material selection based on established limits. In recent years, many developments have taken place in refining the calculation of CO₂ corrosion rates. Furthermore, the definition of 'sour service' has been reconsidered and a much wider review of the applicability of various established and new materials for different service conditions has been made. Increased attention is also being given to life cycle costing (LCC) in the process of material selection.

The present paper considers the corrosion risks that may arise downhole, summarises the options available for corrosion control, and describes some field experience with materials that have been used in various corrosive conditions. In particular it focuses on the increasingly aggressive (i.e. deep), high pressure/high temperature (HP/HT), H₂S containing downhole environments that have to be developed in the coming period. There is no fixed definition of a HP/HT field, but conditions above 500 bar and 170°C are indicative of the conditions that might have to be handled.

ESTABLISHING CORROSION RISKS

Water wetting

The majority of production tubing is made of low alloy steel according to specification API 5CT. For corrosion to occur there has to be water in contact with the metal surface. In many cases, particularly in oil wells, an analysis of the flow regime can show that there will be no direct water wetting of the steel surface and so no corrosion will arise. Indeed, in the 'early days' of plentiful and cheap oil it was not unknown for wells to be shut in once the water content exceeded a certain percentage of the fluid flow (the water cut), so corrosion was rarely the limiting factor on tubing life.

In gas wells, condensation of water occurs when the gas temperature drops below its water dewpoint temperature which may be at a particular height in the tubing depending upon the temperature profile.

In liquid full tubing containing oil and water mixtures, 'free' water may be contained within an oil emulsion and will not give rise to corrosion as long as the flowrate is sufficient to entrain the water and give a continuous oil film at the surface. The amount of water that may be entrained can be determined experimentally and depends upon the type, viscosity, and temperature of the oil. In extreme cases, oils have been found that are capable of carrying more than 90% water in an oil emulsion. Light gas condensate does not offer the same protection as oil and in general does not entrain water, so that water wetting is likely even at very low water cuts.

In multiphase (gas-liquid) conditions the wetting behaviour depends strongly on the flow regime. This is influenced by the gas/liquid ratio, production rates, and the angle of inclination of the tubing.

CO₂corrosion

In considering the feasibility of using carbon steel, the potential general corrosion rate by CO₂ has to be calculated. Laboratory work on CO₂ corrosion has continued to be very active throughout the last five years and has yielded interesting developments and refinements in the modelling of CO₂ corrosion. Several methods now exist for predicting the CO₂ corrosion rate of carbon and low alloy steels, and these have been brought together in one publication of the European Federation of Corrosion (EFC).

The engineering aspects of production tubing design preclude the use of a 'corrosion allowance', to be 'sacrificed' over the life of the project, as this would increase the weight of the tubing string. Thus, where the calculated corrosion rate is judged to be too high to allow the use of
carbon steel, consideration can be given to inhibitor injection to reduce the rate or to the selection of a tubing material that is resistant to corrosion.

**Corrosion in H₂S**

In the presence of H₂S, metallic materials suffer corrosion which leads to hydrogen generation and subsequently a variety of hydrogen induced embrittlement and cracking problems that can potentially cause catastrophic failure. Pitting corrosion of low alloy steels can also occur under certain conditions of temperature, flowrate, and ratio of CO₂ to H₂S.

The resistance of carbon and low alloy steels to sulphide stress corrosion cracking (SSC) has been shown to be dependent not only on the partial pressure of H₂S but also on the pH of the environment. Figure 1 illustrates the influence of pH: region 1 is the domain where SSC is very unlikely to occur and normal homogeneous materials, up to P110 in strength level, exposed to the conditions in this domain do not require any special restrictions; region 3 is the domain where SSC may occur in susceptible materials and special restrictions in terms of hardness or strength or qualification in corrosion tests are deemed necessary; region 2 is a transition region where not fully qualified materials may be acceptable provided they meet fitness for purpose criteria. Where there is doubt about the criticality of the application, then region 2 will be regarded as part of region 3. In the absence of reliable field measurements of pH, approximate pH values can be derived from Ref. 4. Requirements for materials for use in regions 2 and 3 are given in Ref. 3.

For corrosion resistant alloys (CRAs) which may fail in H₂S service by a combination of mechanisms involving SSC and SCC there is no simple cutoff in H₂S partial pressure that can be used to define the limits of risk of cracking. Each type of alloy has to be considered individually.

**CORROSION CONTROL OPTIONS**

The means by which corrosion can be prevented in tubing can be subdivided as follows:

(i) corrosion inhibition of carbon steel
(ii) internal plastic coating
(iii) fibre reinforced plastic (FRP)
(iv) solid CRAs
(v) CRA cladding or lining.

The selection of the most appropriate option is helped by the use of material selection guides, a knowledge of the past field experience and by use of techniques such as I.C.C. and risk analysis.

**Corrosion inhibition of carbon steel**

Corrosion inhibition in its various forms is successfully used in many fields. In some cases the success of inhibition can be attributed to the wells being low pressure, low temperature oil wells with little water.

There are two main methods for injecting inhibitor into a well stream. The first method is to inject down a dedicated treater string enabling continuous injection, and the second is to bolthole at periodic intervals down the tubing with the well shut in. The former is by far the most effective and is potentially suitable for deep, HP/HT, hostile wells.

One major problem associated with traditional inhibitors is that they do not condense on to the tubing wall until high up the tubing string where the temperature is sufficiently reduced. This problem was experienced by Shell, where P105 tubulars have been known to fail after six months in high temperature wells. More work is required before an effective high temperature corrosion inhibitor is available.

Currently, organic based inhibitors are not recommended for temperatures above 150°C, but extensive performance testing under specific operating conditions may allow their use at up to about 170°C in certain cases.

Inhibitors for batch treatment are available but are not very effective at high temperatures. Problems experienced include the increased risk of scaling owing to the carrier water, increased hydrostatic pressure on the well, foaming, and emulsion problems, especially in deep hot wells.

Corrosion control through the use of inhibitors is not recommended for hostile wells because:

(i) the track record for long term protection is poor for HP/HT wells; inhibitors should at least prolong the tubing life to the period between workovers and this has often not been possible for HP/HT conditions

(ii) this option has high operating cost implications over the full field life owing to the operating costs of inhibitor injection and the higher frequency of workovers (on a life cycle cost basis)

(iii) there are concerns about the efficacy of inhibitors in controlling sulphide stress cracking in carbon steels.

**Internal plastic coatings**

There have been widespread applications of plastic coating, many (particularly in more aggressive conditions) with unfortunately short lives. The Phillips EkoFikwells with low levels of H₂S, 90 lb in⁻² (1 lb in⁻² = 6.9 kPa) CO₂, and up to 30,000 ppm chloride levels were completed with N-80 tubing. Even with batch inhibition, the tubing lasted only 19 months before it became perforated, and therefore an extensive coating programme was undertaken. Where no inhibitor was injected, the coated tubing still only lasted about 19 months. Plastic coating on N-80 pipe with inhibitor batch treatment every 30 days gave a tubing life of 7 years. The coating was not always successful, with 15% of the tubing being blistered after only 30 days production.

Coatings were applied to tubing used in deep, HP gas wells operated by the Mitchell Energy Corporation in Southern Louisiana. The shut in bottom hole pressure (BHP) and shut in bottom hole temperature (BHT) were up to 17,500 lb in⁻² and 190°C respectively, with up to 3.5 lb in⁻² H₂S and 1000 lb in⁻² CO₂. The phenolic coatings did not give adequate protection for the severe environment. In one case the coated carbon steel tubing
was subjected to a batch inhibition treatment at 0, 6, 12, and 18 months after which inhibition was stopped. Eighteen months later the casing was pressure tested and a large hole was found in the tubing. Throughout Southern Louisiana and East Texas, operators of HP/HT fields have consistently tried plastic coating and failed.

The use of coating is not recommended for hostile well completions because:
(i) there is a risk of holidays in the coating with the risk of localised corrosion
(ii) phenolic coatings are only rated at up to 200°C and the film thickness at high temperatures and pressures is very critical; thick coatings (above 0.2 mm) may delaminate, especially with rapid depressurisation; thin coatings, however, have greater risk of holidays
(iii) there is increased gas diffusion through the coating at higher pressure, resulting in the risk of corrosion at the steel interface; the corrosion products formed may cause further blister damage
(iv) the track record of coatings as corrosion control barriers has been poor
(v) weldline and caliper surveys is coated tubing tend to damage the coating
(vi) the coatings tend to have low chemical resistance to stimulants and cleanout fluids.

Fibre reinforced plastic
BP Aramco currently has about 9000 wells completed with fibreglass tubing in the USA. Fibreglass is favourable as a tubing material because of its corrosion resistance.5 This type of tubing (to API 5LR) has traditionally been used in linepipe applications where the internal pressures have been below 1000 lb in.2

At higher pressures the tubing is prone to creep, which results in tubing failure before its design life is reached. This is especially true in high temperature applications as the creep is proportional to temperature. Creep is also the reason why this type of material proves to operate very poorly under cyclic conditions. Saudi Aramco has tried FRP for some shallow casings/liners but had corrosion problems between the casing and H2S.

The use of fibreglass tubulums in aggressive environments seems to be somewhat limited and this option is not recommended because:
(i) the most common application is in low corrosion, low temperature (<120°C, and low pressure (<5000 lb in.2) wells
(ii) there are problem areas such as connections, certification, compatibility with other components, and creep resistance.

Glass reinforced epoxy lined low alloy steel tubing is being increasing use. This type of product does not have pressure limitations, but does have a temperature limit (reported variously to be between 80 and 120°C), making it unsuitable for HP/HT wells.

Corrosion resistant alloys
The most commonly utilised CRA is AISI 410 stainless steel (30Cr). Other alloys that have been used for tubing include duplex stainless steels, alloy 28, alloy 825, alloy G3, and C276. The shift from one alloy to the next is made according to guidelines on the performance of these materials in environments of increasing severity. The aim of the corrosion engineer is to select the most cost effective alloy on the basis of an analysis of the corrosion risks in the given environmental conditions.

Correctly selected CRAs should show negligible general corrosion and no localized corrosion or cracking tendency in the anticipated service conditions. CRAs have been widely and successfully used for production tubing in HP/HT wells worldwide. Much of the experience is in the USA and is fairly well documented.

Thus, CRAs are the recommended corrosion control option for hostile well conditions because, with correctly selected materials:
(i) corrosion (general, localised, and cracking) is prevented
(ii) there is extensive past experience
(iii) there is a wide supply capability
(iv) technology is well established
(v) they eliminate workovers due to corrosion failures.

A further advantage of CRAs is that the elimination of inhibitor reduces the operating costs, the space required for the inhibitor tank and pump (where space is at a premium), and the need for operators (critical for remote, normally unmanned developments). These factors may often outweigh the higher capital costs of the tubing compared with carbon steel.

CRA clad tubing
CRA clad (full metallurgical bonding between CRA and backing steel) and lined pipes may be produced by a number of different processes described elsewhere.3

In principle, any clad or lined pipe product is suitable for application as downhole production tubing, although, in practice, there are technical limitations in optimising the corrosion properties of the CRA along with the mechanical properties of the backing steel. Another key problem area is that the tubing has to be joined by special threaded connections which give a leak free seal. This mechanical connection, which is of a standard design, requires development to accommodate the internal cladding or lining.

A prototype lined downhole tubing made by Kawasaki Heavy Industries by a thermomechanical process had the outer surface threaded to provide the tubing side of the joint. The connection was originally designed so that the central part, which was exposed to the production fluids and which mates with the tubing sealing face, was made of corrosion resistant alloy.4

There has been rather little service experience with clad or lined tubing to date, although many operating companies continue to express an interest in this type of product for future developments. Several tests were carried out by Shell, which concluded that, while the use of such production tubing was feasible, more development effort was required, especially in the area of the connection.7

Among alternative technologies that are available, it is worth noting that a research programme in Japan investigated the possibility of chemical vapour deposition, physical vapour deposition, and plasma spraying of the internal surface of downhole tubulars.8 These products are not yet being developed in full size tubing and at present only initial testing of the properties of the coated surfaces has been carried out.

An evaluation of plasma transfer arc weld coated tubulars was made in 1993.11 The tubing specimens were coated with an alloy of composition similar to alloy C276. Hydrogen disbonding tests were carried out and showed a limited amount of disbonding in just two out of the eight specimens investigated. The disbonded regions were of small size (typically 10 mm in diameter) and were found to be sites where there were inclusions or internal contamination at the steel/CRA interface. Critical pitting temperature (CPT) tests in simulated H2S-CO2-brine environments gave a CPT value of 177°C for as produced surfaces with pits tending to initiate at overlapping weld passes or surface spatter. If the surface was lightly machined to remove spatter from the surface, the CPT value increased to about 204°C which was comparable to wrought alloy C276.

Again, this technology has not developed to the production of full size tubing.
APPLICATION LIMITS FOR CRAs IN PRODUCTION ENVIRONMENTS

While typical CRAs used in the oil and gas industry tend to be fairly resistant to corrosion in the presence of CO₂, they are limited in the maximum temperature to which they can be exposed before localized pitting corrosion occurs in the presence of H₂S and chloride ions. There is also a risk of stress cracking beyond certain limits of H₂S, although this is chloride content, temperature, and pH dependent for the different types of alloys. Because of the interdependence of several variables, it is often easier to represent the safe regimes for use of certain materials in graphical form.

In the case of martensitic CRAs the greatest susceptibility to cracking (SSC) is at ambient temperatures which will determine the maximum allowed limits of H₂S. Similarly, the duplex stainless steels tend to show maximum sensitivity to cracking around 80-100°C (a combination of SSC and SCC) which will therefore define the maximum level of H₂S that can be tolerated by the limit of cracking at this temperature. In both cases the maximum service temperature is higher and is the temperature at which pitting or general corrosion rates become too high. Application limits for austenitic materials (stainless steels and nickel-base alloys) are based on their high temperature performance when there is maximum risk of cracking (SSC) and pitting corrosion.

The environmental limits for a selection of materials commonly used in oil and gas production are given in Table 1. Where no value is given there is no known limit within the range of normal operating conditions. In several cases the data given represent 'pass' information, i.e., the actual limit is above these values but has not been determined. Thus, this table should be updated as more information becomes available. The materials are identified in generic groups where possible.

In certain cases it would be possible to use materials outside the stated limits, particularly where there are 'pass' data, assuming satisfactory performance could be demonstrated by testing according to a recommended protocol. Such a test protocol could be used to qualify a material for a specific set of field conditions, simulating the expected brine composition and pH where known, in order to optimize material selection. It is particularly recommended to verify alloy performance by testing when conditions are extreme or when the alloy is recently developed. Note that, for the heat treatable nickel alloys, the control of the heat treatment is critical to the cracking resistance.

From Table 1, general guidance on the application limits of various classes of materials can be derived as given in

Table 1: Environmental limits for selection of materials commonly used in oil and gas production

<table>
<thead>
<tr>
<th>Material</th>
<th>Material Type</th>
<th>Temperature, °C</th>
<th>%NetCl</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>9Cr/1Mo</td>
<td>grade 80, 552 MPa</td>
<td>150</td>
<td>5</td>
<td>Max. temp. depends on chloride and CO₂ content; see Fig. 2 (Ref. 14)</td>
</tr>
<tr>
<td>13Cr 3.5Mo</td>
<td>ER 150</td>
<td>5</td>
<td>3 &lt; pH &lt; 3.5 (Ref. 2)</td>
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</tr>
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<td>15Cr 6Ni</td>
<td>ER 90</td>
<td>2</td>
<td>Ni &lt; 0.2% (Ref. 2 and 15)</td>
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</tr>
<tr>
<td>17-4PH</td>
<td>150</td>
<td>0.01</td>
<td>Limit of H₂S is function of chloride content (Refs. 16 and 17)</td>
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<tr>
<td>17-7Mo</td>
<td>200</td>
<td>0.05</td>
<td>Up to 210°C at lower chloride content (Ref. 18)</td>
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<tr>
<td>17-7PH</td>
<td>200</td>
<td>0.05</td>
<td>(Ref. 19)</td>
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</tr>
<tr>
<td>17-7PH</td>
<td>25</td>
<td>0.01</td>
<td>(Ref. 20)</td>
<td></td>
</tr>
<tr>
<td>with Ni &gt; 37%</td>
<td>25</td>
<td></td>
<td>NKK data</td>
<td></td>
</tr>
<tr>
<td>2Cr</td>
<td>25</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>3CrMo</td>
<td>3.5%</td>
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<tr>
<td>3CrMo</td>
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<td></td>
</tr>
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<td>150</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>15CrMo</td>
<td>300</td>
<td>2.5</td>
<td>No cracking in absence of acetic acid (Ref. 28)</td>
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</tr>
<tr>
<td>15CrMo</td>
<td>350</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15CrMo</td>
<td>400</td>
<td>2.5</td>
<td>No apparent restrictions within normal operating temperature range</td>
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<td>15CrMo</td>
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<td></td>
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<td>900</td>
<td>0.05</td>
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<tr>
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<td>1000</td>
<td>0.5</td>
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<td></td>
</tr>
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<td>1</td>
<td></td>
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<td>15CrMo</td>
<td>1100</td>
<td>1.5</td>
<td></td>
<td></td>
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<td>2.5</td>
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<td>15CrMo</td>
<td>1250</td>
<td>3</td>
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<tr>
<td>15CrMo</td>
<td>1500</td>
<td>5.5</td>
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</table>
Suggested limits of application of 13Cr in absence of H₂S (Ref. 14)

Suggested limits of application for duplex and superduplex stainless steels (pH < 4) (Refs. 20 and 21)

Suggested limits of application of alloy C276 (Ref. 14)

below, but, for specific applications, reference should be made to the details given in the table or additional data sources and individual judgement should be exercised.

Summarizing the results of the various tests for the martensitic stainless steels (9-15Cr), they may all be used generally up to 90°C (9Cr and 13Cr) or 150°C (super-13Cr and 15Cr). The amount of H₂S to which they can be exposed without cracking is critically dependent upon the pH of the environment and also on the chloride content.

The limiting levels of H₂S to which the different types of duplex stainless steels can safely be exposed is given by the values at 80°C in the table, but these are dependant upon the chloride content and pH. Limiting service temperatures are probably around 200°C for environments containing H₂S, and otherwise 250°C, depending on the chloride content.

For the other material types listed in the table, the limiting conditions depend on the maximum temperatures quoted and may be affected by pH, chloride content (particularly for the less highly alloyed materials), and condition of the material (heat treatment or level of cold work).

**PERFORMANCE OF CRAs IN OTHER ENVIRONMENTS**

Care should be taken that the materials selected are resistant to the conditions that may arise outside of the stated design conditions since the risk of failure in these conditions is often overlooked. Procedures should be carefully followed during storage and precommissioning to keep equipment clean and dry (or drained). Severe corrosion or cracking can arise during acidizing, when the environment may be temporarily highly aggressive to the metal, so correct selection of inhibitor by testing compatibility at the acidizing temperature is advised.

Compatibility with completion fluids is another key issue since some of these (particularly the heavier brines) can be severely corrosive to CRAs at high temperature.

**EXAMPLES OF FIELD EXPERIENCE WITH CRAs**

**Solid CRA tubing and casing liners**

Martensitic stainless steel 13Cr has been used extensively in the Tuscaloosa trend (low H₂S, high temperature) with good success, although some pitting corrosion has been observed. One operator, Chevron, has a policy of continuing to use the lightly pickled 13Cr joints until they deem it necessary to replace them.

Austenitic stainless steels have been used in more aggressive environments. In Texas, Santero 28-110 12_/8 in tubing had been in use for some years where there is 75 ppm H₂S, 15% CO₂, a BHP of 16 000 lb in² and a BHT of 212°C with the presence of chlorides. The tubing had been in service since 1981 and was one of the first quoted uses of the material for tubing in the USA. Another example, also in Texas, is the deployment of Santero 28-125 12_/8 in tubing in a well with 3% H₂S and 4% CO₂, at a BHP of 15 000 lb in², a BHT of 165°C, and 1 7% CI⁻. The material has been in service since 1984.

Duplex stainless steels have been widely used. For example, Tenneco has used duplex steels to a large extent in offshore Louisiana (SAF2205) where the closed-in tubing head pressure was 20 000 lb in² with 50 ppm H₂S and high CO₂ partial pressure. Conoco has also used duplex steel in conjunction with 13Cr in East Texas wells (4.5% CO₂, 24 ppm H₂S). Up to 190°C, 13Cr steel was used as it provided sufficient corrosion protection against a corrosive environment comparable with that in the Lower Cotton Valley, and above 190°C SAF 2205 steel was used.

Some companies such as Off Aquitaine discourage their use in deep applications under high temperatures and high partial pressures of H₂S and CO₂ in the presence of large amounts of saline formation water. In such circumstances, nickel alloys with at least 30-40% Ni would be used.

SAF 2205 has been used in aggressive environments. In one reported case in West Germany, 12_/8 in 2303-110 tubing
was used in wells containing 4-4%H₂S, 8-3%CO₂, and 8%H₂O at a BHP of 6000 lb/22 and a BHT of 135°C. The tubing was not used in the field, but it has been in service since 1975. Another example is where 2Cr11Mo stainless steel was used in the Netherlands to replace carbon steel lines that were corroded. The sloped liner was fabricated from SAF 2205-65 and used in wells where there was 2%H₂S, 3%CO₂, and 9%CI at a BHP of 1000 lb/22, a BHT of 140°C, and a water/oil ratio of 90:10. The liner has been in service since 1975.

Also Duarte Marine Operating Company used Inconel 825 alloy for the tubing below the packer, but the complication was not without its problems, attribution to the galvanic cell between the Inconel 825 tubing being coupled to the CS5 tubing above the packer. Banacos completed two Kuhn wells with SM2531 tubing in 1991, primarily for enhancement of the production rate compared with carbon steel. The bottom hole temperature was 138°C and the gas contained 1000 ppm H₂S with 6%CO₂.

Exxon has used C-276 extensively in the Mississippi (Snoakover and Norphlet formations), where high partial pressures of CO₂ and H₂S exist. Arcos has also used this material in the North Padre Island. Mobil has used C-276 and C-50 extensively in its Mobile Bay fields where there are over 20,000 ppm chlorides, 200°C, a high BHP of 10,000 lb/22 and high partial pressures of CO₂ and H₂S (500 and 1100 lb/22 respectively). Under similar conditions in the Madden Deep Unit, LL&L's has installed C276 tubing in wells of 23,000 ft depth.

### CRA clad tubing

Past experience includes a full tubing string internally clad with a 3.5 in diameter steel in service with NAM in the Netherlands, and one example where three clad joints were run at the top of a tubing string.22 The experiences in the field range from good to be satisfactory. Although the particular clad was used in after only two years in service owing to the decline of the oil field. It is believed that the tubing has not been pulled for inspection or used elsewhere. A further field test was undertaken by REB in Germany in 1968, which proved to be satisfactory, although the clad shut in pressure with 160,000 ppm Cl⁻ and elemental sulphur at 140°C. The test well has about 30 ft of lined tubing with two connections. The dimensions are 3.5 in diameter with a 7 mm wall of grade L80 tubing and 3 mm of alloy 625 cladding. The tubing was supplied in about 1968, put into service, inspected after two years, and returned to service at that time. Other similar wells in this period utilised carbon steel with inhibitor and sulphur solvents. The experience so far seems to be good, but, if alloy 625 cladding does not prove to be sufficiently resistant, the operating company may consider (solid) alloy C276 for this service in future.

The fact that clad tubing has not seen wider application may be explained by the following key points:

1. (i) there is a risk of damage to the cladding or lining if wireline operations are required.
2. (ii) the connection has to prove its high reliability, as it is the most critical area for the overall integrity.
3. (iii) if the connection is damaged and has to be recoated, there is a risk of not reproducing the same high integrity joint as in the original product (although new joints and pipe would normally be substituted anyway).
4. (iv) the additional 2-3 mm of CRA inside clad tubing (which is not considered in the mechanical strength of the product) reduces the internal diameter relative to a tubing manufactured from solid CRA, which may restrict throughput and increase pressure losses, particularly in small diameter tubing; moreover, the cladding increases the string weight.

(v) the backing steel has to be carefully considered in terms of its weldability and resistance to sour conditions in general, a CR9 or P115 grade is about the maximum strength level that can be produced as a clad tubing. Solid CRAs can be cold worked to achieve much higher strength levels, such as in grades (30-40) (897-965 MPa-Y), and thus a solid CRA tubing would have a different load for the same depth/president rating: this is significant (particularly in deep wells) since the total weight of the tubing will be less for a solid CRA than for a clad tubing.

(vi) economically it seems that clad tubing can only compete with solid alloys in certain sizes and particularly where there is a corrosion need for highly alloyed CRAs.

### CONCLUSION

The guidelines given in this paper provide a framework for assessing the severity of an environment with respect to corrosion and for establishing likely candidate materials for specific applications. As more data from laboratory or field experiences become available, the environmental limits data should be continuously reviewed and refined. Optimum material selection for specific applications may nevertheless often require the testing of candidate materials under the precise field conditions expected in order to ensure that overconservative choices are not made.

There exists a large amount of experience with CRAs on downhole applications. Correctly selected CRAs have a good track record of service, even for hostile, H₂S containing conditions.

Despite the reservations discussed above, it still seems that clad tubing is an underutilised product. Since many companies face future field developments, especially in offshore locations where there is a fundamental need for the use of CRAs in general (whether solid or clad), it would seem appropriate to re-evaluate the potential use of clad downhole tubing. The possible cost benefits of using clad tubing rather than solid CRAs may be very attractive for deep well developments where high pressure and high temperature conditions may be very aggressive, requiring highly alloyed materials to prevent corrosion. Some clad pipe manufacturers are addressing the technical challenges of manufacturing downhole tubing.

### ACKNOWLEDGEMENT

This paper was prepared with the support of the Nickel Development Institute.

### REFERENCES

19. "NKK material selection guide for OCTG", Fig. A1, 1992, Tokyo, NKK Corp.

British Corrosion Journal 1999 Vol. 34 No. 4