Nickel-containing alloy piping for offshore oil and gas production

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INTRODUCTION

An increasing share of world oil and gas production is now obtained from offshore areas. Improving technology is allowing economic production from deposits in increasingly deep waters and severe weather conditions.

Development of such deposits has emphasized the need for equipment giving high reliability and low maintenance costs. A key approach to satisfy this need is by the use of corrosion-resistant alloy material and there has been a marked increase in the use of such material over the last 10 years in the offshore industry. The corrosive environments favoring alloy material are seawater and oil and gas containing carbon dioxide and/or hydrogen sulphide.

Most of the alloy material used is for piping and the purpose of this paper is to consider the technical (including fabrication) and economic factors influencing the choice of nickel-containing alloy piping. Both topside and subsea system (excluding down-hole) applications are considered in stainless steels (standard austenitic, duplex and high-alloy grades), nickel-base alloys and cupronickels. Systems considered include topside seawater and process systems, under-sea alloy pipelines and topside and subsea manifolds.

Reduction of topside weight is important offshore as it gives cost savings by allowing reduction in deck structural steel and jacket steel weights.[1] Use of alloy piping often gives weight and hence cost savings which improves its economics. The value of weight saving varies with each project and can be very significant.

TOPSIDE PIPING

A) Seawater systems

a) Aerated seawater systems

i) General

Offshore platforms use large amounts of seawater for fire fighting, cooling and water injection (to enhance oil recovery), production of potable water, sanitation, etc. The systems to handle this involve large tonnages of piping as well as pipe fittings, pumps, valves, etc.

Early platforms, in shallow areas with mild climates, were built with galvanized steel and cast iron systems. In flowing seawater corrosion rates of lmm/year are commonly experienced in these materials so that after a few years pipe renewals are needed.[2]

As the corrosion rate is related to seawater velocity, design flow rates are usually limited to 2-2½m/sec.

Development of the North Sea area followed early American practice and galvanized steel piping was often used. This proved unsatisfactory because maintenance in the severe weather conditions commonly experienced in the North Sea proved very expensive and the industry turned to systems based on 90/10 cupronickel as used on board ship. More recently, high-alloy stainless steels have been used.

ii) 90/10 Cupronickel* piping – design considerations

In designing systems with 90/10 cupronickel, flow velocity is again a limiting factor as high flow rates can give rise to severe turbulence in areas downstream from short radius bends, partly throttled valves, etc. This can give rise to corrosion-erosion (impingement attack) in 90/10 cupro- nickel. It is essential, therefore, to design systems at flow rates which are acceptable to the alloy even when some turbulence occurs – as this is present to a degree in all seawater systems. The flow rates chosen are those given in British Standard BSMA-18[3].

This standard allows flow rates of up to 3 m/sec in pipe sizes above 100mm nominal bore, i.e. considerably higher than in galvanized steel. This gives both saving in weight and cost as the pipe diameters are significantly less than in a steel system.

The early cupronickel systems were designed in accordance with BS 3351:1971[4] and thicknesses were based on the stress values in this standard. A later amendment adopted ASME Code V111-UG101-Bursting *Test* which required a bursting pressure of 5 times maximum design pressure. As design pressures up to 20 bar are required for fire mains then wall thicknesses up to that required for 100 bar bursting pressure are used.[5,6]

iii) 90/10 Cupronickel – fabrication

The largest diameter piping required by the offshore industry was beyond the size range for seamless piping (normal limit 16") and fabrication from plate using longitudinal seam welds was developed.

The welds are 100% radiographed to ASME Code Section V111 UW51 to give a joint factor of 1.0.[5] 70/30 cupronickel is normally used for the welding consumable as this gives a weld with slightly better corrosion resistance and strength than the parent plate. GTAW, GMAW, SMAW, and SAW processes have all been used but the first three are the most common. In all cases, filler metal is required which contains additions such as manganese and titanium to react with oxygen and nitrogen which would otherwise give porosity in the weld.

Certain impurities which can occur in the alloy can promote heat-affected zone cracking. Reputable manufacturers of the alloy and of welding consumables are aware of this problem and control impurity levels in their products to minimize the risk of cracking.

When plate and welding consumables from such manufacturers are used, then 90/10 cupronickel has good weldability.[7]

iv) 90/10 Cupronickel – experience

Many thousands of tonnes of 90/10 cupronickel piping have been supplied to the offshore industry during the last 15 years. Where these systems were designed and fabricated in accordance with the standards and recommendations given above and have used valve, pump, etc. materials compatible with the piping,[8] they have performed well and failures have been minimal.[9,10] Reference[10] records only nine cases of failure over a 20-year period, mostly caused by excessive turbulence and polluted seawater during service or commissioning.

Figure 1 shows 90/10 cupronickel for use in seawater hyperfilters on an offshore platform.

v) Stainless steel seawater systems

Interest in the use of stainless steels for seawater systems developed in Norway[11] where, in concrete gravity platforms, which incorporate oil storage/seawater ballast tanks in their base, problems developed in cement-lined steel ballast piping. This piping is alternately exposed to seawater and crude oil containing some sulphides. These conditions caused breakdown and spalling of the cement-linings with subsequent corrosion of the steel pipe.

Although 90/10 cupronickel would have been technically suitable for the seawater exposure, it would be less satisfactory when exposed to sulphide-containing oil. This is because sulphides are incorporated into the films on the alloy making them less protective. A pipe with such a film exposed to aerated seawater can suffer serious corrosion.

Although stainless steels are resistant to sulphides, the standard austentic grades such as Type 316 are prone to pitting and crevice corrosion in chloride-containing waters such as seawater. It was necessary, therefore, to select an improved stainless steel and a 21% Cr 18% Ni 6% Mo + N alloy, was selected.

This decision stimulated interest in stainless steels for seawater systems and a detailed and comprehensive study of a large number of stainless steel and nickel-based alloys has been carried out by Shell.[12] This includes laboratory investigations and pipe system loops to study both materials and components in seawater. This indicates that high-performance duplex and 6% molybdenum austentitic steels are suitable for seawater systems.

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*Details of composition and properties for materials referred to in the text are given in Appendix 1

vi) Stainless steels – corrosion resistance in seawater

Stainless steels exposed to seawater, particularly in shielded areas, are prone to pitting and crevice corrosion. Resistance to this localized attack is improved if the chromium, molybdenum and nitrogen contents are increased. For most austenitic grades, the chromium content is about 20% and at this level, about 6% molybdenum and 0.15% nitrogen are needed to give an alloy virtually complete resistance to crevice corrosion in seawater. Detailed studies on the effect of alloying elements have been carried out by various researchers, notably Oldfield,[13] and a ranking of various alloys can be derived from his mathematical model. However, useful comparisons can easily be made using the *Pitting Resistance Equivalent Number,* PRE $_N$[14] which is usually calculated as follows:-

$$PRE_N = Cr\% + 3.3\ Mo\% + 16\ N\%$$

The higher this number, the greater the resistance to crevice corrosion. The PRE_N indicates the marked influence of molybdenum and nitrogen.

A PRE_N of at least 40 is considered necessary in an alloy to have sufficient resistance in aerated seawater for critical applications such as piping and heat exchanger tubing.

PRE_N for some stainless steels are given in *Table* 1 and *Appendix 1*

Table1
Pitting resistance equivalent number nominal composition

Alloy	Cr%	Mo%	N%	Ni%	Other%	PRE$_N$
UNS S31603	17	2.5	-	12	-	25.25
UNS N08904	20	4.5	-	25	1.5 CU	34.85
UNS S31254	20	6.0	0.2	18	0.8 CU	43.0
UNS N08925	21	6.0	0.15	25	-	43.2
UNS N08367	21	6.5	0.2	25	-	45.65

General corrosion of stainless steels in seawater is extremely low and no corrosion allowance is necessary.

In fast flowing seawater, stainless steels remain passive and provided cavitation is avoided, the surface remains unattacked at velocities well above those used in piping systems. *Table 2* provides data on some standard austenitic grades; the results are typical for all stainless steels.

Table 2

Stainless steel grade	Seawater velocity m/s	Corrosion rate microns/year
304	43	5
316	43	5
Alloy 20	41	15

vii) Stainless steel seawater systems – design considerations.

Based on the corrosion data in *Section vi)* it is clear that the main corrosion consideration influencing the selection of stainless steel seawater piping is resistance to crevice corrosion as both general corrosion and corrosion-erosion losses are negligible. Also, stress-corrosion cracking is not a problem as ambient temperature seawater does not reach the

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widely accepted 60°C temperature limit below which cracking does not occur.

Table 1 indicates that materials such as UNS S31254, N08925 and N08366 should be suitable for seawater systems and extensive use has been made of Avesta 254SMO* (UNS S31254) in two Norwegian projects.

In designing these systems, account was taken of both the high flow resistance and high strength of the alloy to reduce both pipe diameter and thickness.

Pumping costs increase with flow rate and a compromise between reduced pipe cost and increased pumping costs is necessary. Statoil, Norway, designed their systems at 7m/sec – this limit also being influenced by the noise generated by the flowing seawater.[15]

For design, allowable stresses were based on Norwegian Code TBK6 which allows a safety factor of 2.4 for UTS and 1.35 for yield stress compared with 3.0 and 1.5 respectively for ANSI B31.3. For UNS 31254 this allowed a design stress of 170 N/mm^2 for TBK6 compared with 153 N/mm^2 for ANSI B31.3.

viii) Stainless steel seawater systems – service experience

Although small amounts of 6% Mo stainless steels have been used satisfactorily in various offshore applications since 1979, the first major usage was in the Gullfaks and Osberg fields in Norway. Approximately 5000 tonnes of Avesta 254SMO piping has been used for those fields and performance has been satisfactory. The first platform – Gullfaks A – was installed in 1986.

The effect of high flow rate and design stress on the size and weight of two pipe system components is shown in *Table 3*.

Figure 2 shows part of the fire system in Avesta 254SMO on Gullfaks A.

A more recent development has been the use of a duplex stainless steel for a United Kingdom project – Amerada Hess, Ivanhoe and Rob Roy fields. The alloy selected is Zeron* 100 (24% Cr 4% Mo 0.2 N 0.8% W 7% Ni). This alloy has a PRE_N over 40 and consequently should have sufficient corrosion resistance for pipe systems handling aerated seawater. These systems have recently entered service.

There are now several of these high-performance duplex alloys available in wrought and cast form, e.g. SAF 2507, Fermanel*, Uranus* 47N, Sumitomo DP3*, etc.

b) Dearated seawater systems
i) General

Many offshore platforms are fitted with water injection systems to improve the production profile of the field and to increase oil production. These systems require large volumes of water which must be filtered and treated to remove bacteria such as sulphate reducers that could cause the field to go sour.

Oxygen is also removed to reduce the corrosivity of the seawater.

These systems operate at high pressures (100* bar) and corrosion rates must be low or mechanical failure would result.

Table 3

	Stainless steel			Cupronickel		
	Size	Wall thickness mm	Weight tonnes	Size	Wall thickness mm	Weight tonnes
Seawater lift discharge from pumps: 6m pipe + 3 flanges and 1 valve per pump.	14"	4.78	2.7 (d)	20"	7.5	5.8 (d)
	14"	4.78	5.5 (w)	20"	7.5	11.5 (w)
Seawater lift header 180m straight pipe	20"	6.35	18.7 (d)	36"	8	37.7 (d)
	20"	6.35	77.9 (w)	36"	8	151.7 (w)

* (d) = dry
(w) = wet

ii) Corrosion in deaerated seawater

The authors[16] have published a detailed study of corrosion of carbon steel and stainless steels in deaerated seawater. *Figure 3* from this study shows how corrosion rate is influenced by oxygen content and flow rate in a 150mm diameter carbon steel pipe. This shows that high corrosion rates can occur at moderate flow rates (2 m/sec) at less than 50 ppb oxygen. For acceptable corrosion rates, deaeration to oxygen levels below 10 ppb is necessary. Also, for high flow rates, such as are experienced in pumps and partly throttled valves, corrosion rates on carbon steel are unacceptably high and alloy materials should be used.

Stainless steels are resistant to pitting and crevice corrosion in deaerated seawater as, at neutral pH, these phenomena are dependent on the setting up of differential aeration cells. At low oxygen levels, such cells are ineffective. *Table 4* provides data for natural aerated (typically 8ppm) and hot deaerated seawater for Type 316 stainless steels.

In considering corrosion in deaerated systems, attention must be paid to the presence of other oxidizing species in the seawater, notably chlorine. It is common practice to add a biocide to seawater after deaeration. If chlorine is used for this treatment it will, from the corrosion viewpoint, have a similar effect to adding oxygen and severe corrosion can occur[16]. A nonoxidizing biocide is preferred for deaerated seawater.

iii) Deaerated seawater systems – materials selection.

A water injection system consists of lift pumps, piping valves, etc. coarse and fine filters, a deaeration tower, up to the deaerator, is similar to the seawater systems described under Topside piping and the same alloy material selection is advised, i.e. 90/10 cupronickel or 6% Mo austenitic stainless steel. Materials for pump, filters, etc. should be compatible with the chosen pipe material.

After deaeration, which is achieved physically (in the deaerator) and chemically (by addition of sulphite or bisulphite), the corrosivity of the seawater is greatly reduced. Piping in carbon steel can be used, provided the oxygen level is low (see *Section i* above) but where high flow rates are experienced, then stainless steels are required, for example, in pumps, valves and reducers. Because of the high pressures, duplex stainless steels are often used for larger components as their high strength allows significant weight saving. Proprietary higher alloy duplex stainless steels are often used for injection pumps as they have higher resistance to pitting and crevice corrosion – examples are Ferralium* 255-3SC, Noradur*, Zeron 25 and 100, etc.

B. Process pipework
(a) General considerations

Compared with a decade ago, the increased amount of corrosion-resistant steels and alloys now being used for topside process piping and vessels, replacing carbon steel with substantial corrosion allowances and inhibitors, is quite remarkable.

The economics of the use of corrosion inhibitors offshore is entirely different to that for onshore installations. The life-cycle cost of inhibition is high in offshore usage since inhibitor cost, storage and transportation costs all have to be taken into account as well as manpower for supervision and maintenance of injection equipment. Since reduction in topside weight is a key aim of offshore engineering planning in order to save on supporting structure costs, the additional weight associated with inhibitor usage and the substantial

Table 4,[13,17]

Corrosion of Type 316 stainless steel in aerated and deaerated seawater

Environment	Exposure time days	Velocity m/sec	General corrosion or pitting
Natural N. Atlantic seawater	486	0	2.4mm P
Deaerated seawater 105°C 25 ppb O_2	547	0	0.12mm P
Natural N. Atlantic seawater	30	37	0.009mm/yr G
Brine pH 7.8 25 ppb O_2 at 50°C 133000 ppm CL.	8	40	0.027mm/yr G

P – Pitting   G – General

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corrosion allowances on carbon steel piping still required, is not insignificant. Furthermore, inhibitors, whilst generally effective in controlling wet gas corrosion at low temperature and low velocities, frequently exhibit unreliability at higher temperatures, higher fluid velocities, or with turbulent flow regimes; particularly when sand is present, which is not uncommon in North Sea fields. On the contrary, standard and special austenitic steels, and various medium- and high-nickel alloys have good erosion/corrosion resistance in wet gas streams under comparatively high velocity conditions. In some circumstances, with the use of corrosion-resistant alloys, it is frequently feasible to reduce the pipe size, thus permitting significantly higher velocity flow, but with considerable savings in pipe weight, including corrosion allowance savings. In one typical piping system on a North Sea platform, it was possible to achieve more than a 50% weight saving by replacing carbon steel with smaller diameter duplex stainless steel (UNS S31803); in this case the fluid velocity was allowed to increase from 6 to 11 metres/sec and a 3mm corrosion allowance eliminated.

There may be an environmental cost associated with inhibitor usage since the inhibited water phase is separated from oil and gas and discharged to the ocean. Environmental requirements in some locations may dictate waste water treatment to remove amines and other inhibitor chemicals.

Also, when alloy production tubing is used (e.g. duplex stainless steel or 13% Cr steel) without inhibitors, there is less incentive to provide an inhibition system solely for process piping.

Basically, the major processing operations carried out on platforms consist of separation of oil, gas and produced water, drying gas, recovery of chemicals such as methanol, glycol added for suppression of hydrate formation, flaring gas, etc. Gas compression for reinjection or export is often required.

Flare systems involve low temperature design for blow-down conditions when pressure reduction and condensate evaporation can give rise to low temperatures, and ferritic nickel steel (3 % Ni steel), austenitic stainless steel and duplex stainless (>-50°C) are used to provide low-temperature toughness.

(b) Material selection – assessment of corrosivity of fluids.

The principal factors affecting corrosion rates of carbon steel in gas and oil process streams can be summarized as follows:

Gas	Oil and gas
pCO_2	pCO_2
pH_2S (Sour gas)	pH_2S
Gas/condensate/water ratio	Oil/gas/water ratio
Chloride content of water	Chloride content of water
pH of water	pH of water
Oxygen content	Oxygen content
Flow velocity regime	Flow velocity regime
Temperature	Temperature

It is not proposed to deal at any length with the detailed effect of the various factors on carbon steel, these being well covered in the literature.

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As far as the stainless steel and nickel alloys are concerned, the principal factors governing general and localized corrosion, chloride stress corrosion cracking and sulphide stress cracking are pH_2S, pH, chloride content, temperature and oxygen.

Crolet and Bonis[19] have carried out pH measurements at high pressure, demonstrating the importance of taking account of pH of water phase as well as pH_2S in defining SCC potential. This highlights how pH can vary markedly with detailed water composition and they developed a computer program for calculating pH of formation waters, verified by high pressure pH measurement.

pH is a major factor affecting the threshold temperature for chloride stress cracking of stainless steels and pH_2S threshold for materials susceptible to sulphide stress cracking. The virtual absence of oxygen in produced well fluids significantly reduces propensity to pitting, crevice corrosion and chloride stress corrosion cracking of austenitic and duplex stainless steels and higher nickel alloys. It follows that oxygen ingress into process streams is deleterious.

Madsen et al[20] describe corrosion test in brine containing CO_2 and $CO_2 + H_2S$, with and without 2 ppm O_2 in connection with the qualification of duplex stainless steels for a North Slope Alaska project. The effect of oxygen is clearly demonstrated.

The NACE standard MR0175-88 is followed for defining risk of sulphide corrosion cracking and gives restrictions on material properties and heat treatment (e.g. hardness) for sulphide service. This standard has generally proved very effective in controlling SSC but there is considerable controversy in the application of this standard with some materials, e.g. duplex stainless steel, referred to later.

One of the problems facing oil companies in selecting materials and corrosion protection systems for topside equipment is that over the projected life of a field there is a possibility that the corrosivity of the produced fluids may change significantly. Water flood stimulation using deaerated or partly deaerated seawater is extensively used in the North Sea and in consequence the composition of the produced water and is corrosivity may change. In the later years of its life a sweet well may become sour, the H_2S being formed by the action of sulphate-reducing bacteria introduced with injected water in spite of efforts to control the initial introduction of bacteria and bacterial nutrients. Prediction of such changes is extremely difficult, yet such considerations, particularly if conservative, can influence markedly initial materials selection.

There is a considerable variation within the industry in the assessment of corrosivity of oil and gas process streams, criteria for acceptance of corrosion rates, attitude to inhibitors vs corrosion-resistant materials, emphasis on initial cost rather than total cost. Smith and De Waard[21] describe the philosophy of a major oil company in assessing the corrosivity of production environments, applying their selection criteria and the use of a spreadsheet program to match the input data with established limitations on commonly used materials, based on their own operational experience, published data, in-house and published laboratory test data and providing material recommentations as output.

Materials for topside piping applications
(a) 3 % Nickel steel

Piping in 3 % Ni steel has been used for low-temperature piping (-50 to -100°C) in flare systems on several North Sea platforms where corrosion in not a problem and the nickel content limitation for sour service in MR0175-88 does not apply. In flare systems and other high-pressure process piping systems, blowdown conditions can result in pressure release and condensate evaporation, resulting in low temperatures that must be taken account of in material selection and design. Matching composition welding consumables can be used for temperatures down to about -75°C and high-nickel alloy electrodes (AWS E Ni Cr Fe 2/3) for temperatures down to -100°C.)

b) 316L Austenitic steel

Of the standard 300 series stainless steels, 316L is the grade most widely used for pipe and tubing on offshore platforms. Because of the fact that well fluids are devoid of oxygen, unless ingress of oxygen occurs during processing, 316L performs quite well in terms of pitting, crevice corrosion and chloride stress corrosion cracking and has been successfully in various services on platforms and in moderate severity corrosion services.

The practical limit of 60°C generally applied to 316L and 304 to avoid SCC in chloride-containing environments may, on account of the absence of oxygen, be regarded as conservative, except when the pH is excessively low, e.g. if the pH_2S is high. It must be remembered, however, that the atmosphere is often salt laden and a high concentration of chloride may form on the external surface of exposed piping or particularly under insulation. Consequently, since oxygen is not excluded from external surfaces it is advisable to apply the 60°C rule of thumb maximum for general use on offshore platforms.

When heavy wall, large-diameter 316 pipe is required in relatively moderate quantitites, some oil companies have made substantial cost savings and improved deliveries by using centrifugal-cast pipe for heavy spool fabrication in conjunction with normal wrought fittings.

c) Duplex stainless steels

Usage of duplex stainless steels, specifically the 22Cr/ 5Ni/ 3Mo/N grade (UNS S31803) for topside piping and vessel application on North Sea platforms has grown markedly in the last five years, in addition to usage for downhole production tubing and subsea flow lines. Its high strength, good general corrosion and pitting resistance, good resistance to chloride SCC and good weldability make it an ideal material for wet CO_2 service in topside processing equipment applications and at a modest cost premium over 316L. It is not susceptible to erosion/corrosion in wet CO_2 environments at velocities considerably higher than those likely to be encountered in topside process piping systems and can be judiciously used to save considerable topside weight compared with inhibited carbon steel incorporating substantial corrosion allowances.

Duplex stainless steel (UNS S31803) welded with 22Cr/ 9Ni/3Mo consumables can meet normal Charpy V require-mants (35J min average, 27J min individual) down to -50°C

and has been used on flare piping systems.

On some recent North Sea platforms, UNS S31803 has been used for piping from the wellhead to after the separators, which in a few cases, have also been specified in duplex stainless steel.

NACE MR0175-88 (Revision) lists duplex stainless steels of UNS 531803 type as being acceptable for sour service in annealed condition providing the hardness does not exceed 28 Rockwell C. However, the publishing of slow strain rate test (SSRT) data by a major oil company[21] has caused considerable controversy; these data *(Figure 5a)* said to be presented in a conservative manner, relate threshold pH_2S limits above which cracking may occur and temperature. The suggested limit for the critical temperature range 50-100°C is of the order of 0.01 bar, which is considerably less than pH_2S limits being considered as practical limits for several North Sea proposals. The controversy centres around the validity of SSRT tests. *Figure 5b* presents data from an equally re-spected source[11] on autoclave static SCC tests on material which had been cold worked to increase yield to 130 ksi, and is therefore also very conservative as far as pipe used in quench annealed condition and welded is concerned. These data obtained with $PCC_2$1000 psi and 15% Na CI concentration with load, at the 0.2 proof strength value for the test temperature clearly suggests much higher practical limits. This controversy, which at the time of writing is far from resolved, does however appear to have influenced material selection decisions on some current projects.

The 25% Cr duplex steel, UNS S31255, has been much less used for topside process piping to date, although cast versions of this type of alloy are virtually standard for water injection pumps. However, in recent years various proprietary modifications of UNS S31255 have been introduced (Zeron 100, Fermanel SAF 2507, etc). The general aim of these modifications is to maximize pitting and crevice corrosion resistance, making use of the positive beneficial effects of N, Cr and Mo contents, according to the useful PRE $_N$ relationship given earlier to attain values of 40+ and trimming with increased additions of nickel to give required austenite-ferrite balance.

One proprietary alloy of this type has been specified for seawater piping and wellhead manifolds and process piping in the UK and Norwegian sectors respectively.

d) High-molybdenum stainless steels

Steels of interest in this category are the 6% Mo steels, e.g. UNS S31254 and UNS N08925 and the 4.5% Mo steel, UNS N08904 *(See Appendix I)*. The 6% Mo steels, particularly UNS S31254 have been extensively used for seawater systems mainly, but not exclusively, in the Norwegian sector of the North Sea and in heat exchangers handling various sweet and sour process streams[21] but have not yet been used to any major extent for topside process piping with the exception of occasional sour water lines. However, very recently 6% Mo steels have been specified for the wellhead manifolds and all piping up to the oil/gas/water separators for a major Norwegian project. This field has a 40-year projected life and in view of concern about ultimate levels of H_2S and chloride content of produced water, the 6% Mo steels were specified in preference to duplex stainless steel UNS S31803. Wallen[21] describes the results of stress corrosion cracking and crevice

corrosion tests on UNS S31254 in simulated sour environments. The 4.5% Mo steel UNS N08904 has been used on a number of platforms in the form of clad heavy-section plate mainly for separator vessels, but also for associated piping.

e) Medium and high-nickel alloys

The materials of major interest in medium nickel alloy category are Alloy 825 (UNS N08825) and Alloy 28 (UNS N08028). In the higher nickel category Alloy 625 (UNS N06625) and Alloy G (UNS N06007) find application.

Alloy 825 has been fairly extensively used for process piping up to and including the separators on a number of oil and gas platforms in the UK sector of the North Sea since the beginning of the decade. It has been used in moderately severe conditions up to 30% CO_2 100 ppm H_2S 500 bar at up to100°C mainly on the grounds of expected good resistance to stress corrosion cracking. Alloy 825 has a relatively low PRE_N and a high Mo (5%) version to improve the PRE_N has been offered but to the authors' knowledge not used. It would appear that Alloy 825 has adequate pitting resistance under the anerobic conditions involved and has given good service.

Popperling[24] reports SCC cracking test data in 5M Na CI with 10 bar H_2S, 20 bar Co_2 170 bar N_2 in which cold worked Alloy 825 (119 ksi) did not[2] crack at loads up to the 0.2% proof stress (at temperature) at exposure temperatures up to and including 200°C, a temperature not likely to be exceeded in normal topside processing applications.

Figure 4 shows test (10") and production (16") manifolds in Alloy 825 for a UK sector oil platform. The manifold run pipe (up to 32mm thick) is in centrifugally-cast Alloy 825 giving considerable cost savings and delivery improvements compared with wrought pipe. Centrifugally-cast Alloy 825 manifolds are also being used on a gas production platform in the southern North Sea and are under consideration for at least one other current project. Cast Alloy 825 differs from wrought Alloy 825 principally in that it is niobium- rather than titanium-stabilized for foundry reasons. Centifugally-cast Alloy 825 readily matches the wrought alloy in 0.2% proof strength but tends to have a lower minimum UTS. However, applying ANSI 31.3 code, which is the code used generally for process piping design, at least in the UK sector the allowable design strength is *yield controlled* and in consequence the cast alloy has identical allowable design stress to the wrought alloy. In ANSI B31.3 a casting factor of 0.8 is applied but this can be raised to 1.0 if the cast pipe is machined inside and out, (normal practice for centrifugally-cast pipe), dye-penetrant tested inside and out and radiographed, in which case cast pipe can replace wrought Alloy 825 without design penalty.

In spite of additional quality control, the cost saving in these instances was very substantial indeed.

The Norwegian specification TBK6 does not specifically mention cast pipe materials but application of their design stress criteria would result in the same conclusion, i.e. it is *yield controlled.*

The refining and petrochemical divisions of oil companies have for many years used centricast alloy piping for critical applications and it would seem that production divisions of some companies are now recognizing there is a niche for centrifugal casting for heavy wall alloy piping spools and manifolds, particularly when only relatively small tonnages of heavy wall, large-diameter pipe is required.

Piping internally clad with Aloy 825 is being considered for process piping applications; tees and bends can be produced from clad pipe and clad weld neck flanges by overlaying techniques. Clad pipe 4" and above can be made by centrifugal casting methods and this will be referred to in the section on subsea lines.

One other application for Alloy 825 is gas turbine exhaust piping, where the chloride in the atmosphere can cause external SCC of less resistant alloys.

Alloy 28 has been quite extensively used in the cold worked condition (120 ksi) for production tubing casing and lines in sour wells in Texas, Louisiana, Florida and the Gulf of Mexico. To date it has not been widely used in the North Sea and north European oilfields, although it is a European development.

It has been used for handling very sour production water in a German field and for chemical dosing pipe systems on North Sea platforms. It is now receiving wider consideration in some companies for severe corrosion service since uncertainty has been created regarding the suitability of duplex stainless steel as referred to earlier.

The high chromium content (28%) in conjunction with 3 % Mo confers good pitting resistance (PRE_N - 39).

SCC tests,[22,24] in simulated well fluids indicate the alloy to have exceptionally good cracking resistance up to 300°C.

A higher Mo variant (6%) has recently been announced and this would be expected to enhance pitting and crevice corrosion resistanace even further.

Major applications of Alloy 625 piping on offshore platforms are not numerous. Extensive use was, however, made of the alloy in piping systems of a molecular sieve drying unit for a combination of reasons:

a) Mechanical design considerations over a relatively wide design temperature range (-70° to +350°C)

b) The need for outstanding general and localized corrosion resistance in aggressive, low pH, high chloride media containing H_2S

c) Resistance to chloride SCC and sulphide SCC sour, high chloride environments.

Alloy 625 has also been used for waste water drains handling low pH high chloride effluent. Alloy 625 has outstanding crevice corrosion resistance in acid chlorides.[13]

It has, however, been extensively used in supplementary applications - e.g., weld overlaying and welding corrosion-resisting alloys. Alloy 625 is exceptionally amenable to overlaying using TIG or synergic pulsed MIG welding which is extensively used for internal overlaying of valves and other components and surfacing of heat exchanger tube sheets, etc. Alloy 615 welding wire and electrodes (ER Ni Cr Mo 3 + E Ni Cr Mo 3) are extensively used for providing weld metals overmatching in corrosion resistance for alloys such as UNS S31254 and UNS N08925, UNS N0825. Its welding behaviour is such that it can be used for heavy section welds, see *Figure 4*. It is recommended for welding wrought Alloy 825 when section thickness exceed about 19mm.

Alloy 625 clad plate is now available which can be converted to large diameter pipe by longitudinal welding; and small diameter Alloy 625 clad pipe can be made by centrifugal casting techniques.

SUBSEA PIPING SYSTEMS

a) General

Alloy materials, usually stainless steels, but sometimes nickel-base alloys, have been used for subsea pipelines and flow lines. Both rigid metal and flexible metal/nonmetal lines have been used.

Manifolds for subsea completions, as well as those on platform topsides, are essentially part of the piping system and are often made from alloy material.

b) Subsea piping – duplex stainless steel

Some gas deposits contain appreciable amounts of carbon dixiode. This can give rise to serious corrosion of carbon steel in areas where water phases are present – sweet gas corrosion. De Waard and Milliams[25] have made a detailed study of corrosion of carbon steel in CO_2/water environments and their work has allowed reasonable predictions of corrosion rates in service to be made.

Although inhibitors are sometimes effective in reducing corrosion in carbon dioxide, in other cases they are either ineffective or uneconomic.

Studies by Milliams[26] showed that chromium-containing alloys had high resistance to sweet gas corrosion and following successful service on land; in-field lines in duplex stainless steel UNS S31803 (W.N. 1.4462 22% Cr 5% Ni 3% Mo + N) were fitted in several of NAM's Netherlands offshore fields.

i) Duplex stainless steel pipelines – economic considerations

Although duplex stainless steel piping is considerably more expensive than carbon steel, other factors enable it to be used economically. These are:

1) The ability to produce corrosive gas from a subsea completion or a simple platform, and to convey it untreated to a process plant, saves platform and equipment costs.

2) Elimination of inhibitors, their storage and injection facilities gives significant savings.

A detailed analysis of the economics of usage on a Dutch field has been published by Groenewoud.[27] *Figure 6* compares costs for stainless steel flowlines with centralized processing, and carbon steel flowlines with drying installations, on each platform and establishes a breakeven distance of 8km for the use of stainless steel. As the actual distances were less than this, two stainless steel lines were fitted.

ii) Duplex stainless steel pipelines – fabrication and installation

Duplex stainless steels are designed to have a microstructure consisting of 50% ferrite and 50% austenite. Weldments should aim to retain a roughly similar balance. High cooling rates, as can occur with low heat inputs, can produce a weld heat affected zone with high (90%+) ferrite content. The weld metal is subject to similar considerations and in order to obtain a weld deposit with an acceptable ferrite/austenite ratio, it is necessary to increase the amount of austenite stabilizer–usually nickel–in weld consumables. Standard consumables have generally been of the 22 Cr/ 9 Ni/ 3 Mo type but there are now trends to higher chromium (25%) high nitrogen (0.3%) to give improved corrosion resistance in the weld bead – (PRE_N 38 approximately). Autogenous welds are best avoided. A high heat input can result in high austenite contents and precipitation of nitrides in the heat-affected zone.

Welding processes are usually restricted to heat input between 0.5 and 2.5kj per mm. As these heat inputs are low in comparison with carbon steels, and specified interpass temperatures are also lower, welding tends to be slow and this increases pipeline costs due to pipe barge rental charges. To reduce time offshore, stainless steel piping is often pre-fabricated ashore into longer lengths. In the case of the Shell Sean and Indefatigable fields, 40-ft. lengths were double-jointed onshore; nevertheless, the 20" lines were laid at only 0.65km/day compared with 3km/day for carbon steel .[26] *(Figure 7)* shows the Sean/Indefatigable line during laying). For short flowlines, welding onshore and towing to site provides an economic alternative to high-cost barge welding.

Because of this high cost of welding there is an incentive to develop alternative methods. One such method is forge welding, e.g. SAG forge welding which is receiving attention in Norway. Another is flash butt welding; to the authors' knowledge, neither has yet been used commercially in the North Sea. *References 30* and *31* give a good review of welding duplex stainless steels.

For small-diameter flowlines, consideration has been given to reel laying of duplex stainless steel; this has not yet been done in practice but is under consideration for laying flow-lines from a subsea production installation to a production platform in the UK sector. Crucial to the performance of the piping is a high quality root run and GTAW welding is normally used. Shielding and purge gas is normally pure argon. Hydrogen additions to the gases must be avoided as this can lead to embrittlement of the material. With a good quality root run in place the joint can be filled with higher production processes such as GMAW and SMAW.

To avoid contamination of the stainless steel surface during fabrication, all clamps, wires, brushes, etc. should be made from stainless steel.

For corrosion protection the piping, after fabrication, is covered with a 4mm layer of polyethylene and a 50mm-thick concrete buoyancy coat. These are put on the pipes before lay-barge welding, only the weld area being left open and covered before laying.

In case of damage to these coatings, which could result in a severe crevice attack in the polyethylene/metal crevice, cathodic protection using sacrificial anodes is usually provided. As the line is normally connected to carbon steel, then the protection potential chosen is usually that for steel, i.e. - 850 my Ag/AgCl. Care is needed to avoid more negative potentials as there is a risk of hydrogen embrittlement in duplex stainless steels .[29]

c) Subsea piping – flexible piping

Flexible flowlines, risers, umbilicals and similar applications have been developed for offshore use.[32] These are

composite structures made up of several layers of different materials which together provide pressure containment, radial and axial strength and external protection.

An inner-metal interlocked steel carcass is provided whenever gas is present and this is usually made from Types 304 or 316 stainless steel and occasionally duplex stainless steel. This layer protects the pipe against collapse from external pressure and prevents wear of the internal pressure layer.

Flexible piping is made in continuous lengths which are stored on drums. The maximum length produced is limited by the capacity of the drum and is also related to the diameter of the piping. The piping is laid by unspooling from the drums.

By altering the thickness of the inner carcass and the armoring, the strength can be adjusted for laying in various depths of water.

Cathodic protection is normally provided to ensure that carbon steel exposed to seawater by physical damage to the outer layers of the pipe will not corrode.

Flexible piping such as Coflexip* is more expensive on a cost per metre basis than steel piping. However, when ease of installation is considered, it competes with steel piping in many applications.

d) Subsea piping – experience with alloy materials

Flexible pipelines have been used in a variety of applications worldwide. Up to the end of 1985, 1280km of these lines had supplied by one manufacturer.[33] At that time about 260km/ year was supplied using 1200 tonnes/year of stainless steel.

Duplex stainless steel (UNS S31803) pipelines have been used mainly in the North Sea. The following table gives details of the main lines.

TABLE 5

Duplex stainless steel pipelines in the North Sea

Dutch sector	Length, km	Diameter and thickness
Platform K8-FA1	5.9	6.625" o/d x 6.2mm t
Platform K11 - FA1	3.8	10.75" o/d x 10mm t
Platform K8 FA3-K7 FA1	9.0	12.75" o/d x 9.4mm t
Ameland	3.0	20" o/d x 14mm t
Platforms LH/LA - LG	10.0	8" o/d x 9mm t
UK sector		
Inde M	4.7	12.75" o/d x 14mm t
Sean N	4.7	20" o/d x 14mm t
Brae Central - Brae A flowlines	7.0	2-6" o/d
Norweigian sector		
Tommeliten	11.5	2-9"o/d x 15.6mm t (production) 1-6" o/d x 25.6mm t (test)

A number of subsea lines in duplex stainless are also currently under consideration.

Duplex stainless steel UNS S31803 has been used for subsea manifolds in both the Norwegian and UK sectors. In one case, in the UK sector, centricast duplex 22 Cr/ 5 Ni/ 3 Mo was used.

There is no published information on problems in the pipelines in service although problems have been reported due to preservice conditions such as hydrotesting with brackish water.[34]

Cathodic protection is normally applied to duplex stainless steel pipelines and the criteria applied are usually those for carbon steel, as explained above. Duplex stainless steels are prone to hydrogen embrittlement under cathodic charging[29] and care is needed to ensure that excessively negative potentials are avoided.

e) Clad piping for subsea service – general considerations

In the last 3-4 years there has been growing interest in the use of alloy-clad piping for risers, flow lines and subsea template piping/manifolds. Potential problems associated with cathodic protection of stainless steel have tended to encourage this interest which has also been stimulated by the controversy about resistance of duplex stainless steels to sour conditions as described above.

The alloys so far used for the clad layer are Type 316L, Alloy 825 and Alloy 625. *Table* 6 summarizes several applications of alloy-clad piping in the North Sea and elsewhere.

Large-diameter clad piping can be conveniently produced from rolled or press-formed clad plate with longitudinal seam welding. For smaller diameter, 6-8" piping, as might be required for subsea manifold template piping and smalldiameter flow lines, clad pipe made by centrifugal casting techniques or explosively bonding alloy liners into carbon steel pipe come into reckoning. The latter method, although very promising, seems to need further development before the degree of bond continuity specified by oil companies can be guaranteed. There has, however, been good experience with clad pipe made by centrifugal casting. Using such centrifugal production techniques, X65 pipe clad with Alloy C276 has been used for flowlines in geothermal station service in the US. Alloy 625 and Type 316L pipe for sour gas flowlines and recently 6" X52 pipe clad with 3mm of Alloy 625 has been produced for a subsea manifold to be installed in the UK sector of the North Sea.

Bends can be formed from clad pipe by induction bending techniques and forged tees have been produced from centricast pipe with Type 316L and Alloy 825 cladding.

Since weld neck flanges can be readily weld overlaid, all the components for construction of internally-clad subsea manifolds, flowlines, risers, etc., are available. *Figure 8* shows a cost comparison of centricast Alloy 825 clad pipe with solid Alloy 825 centricast pipe in the 4"-12" size range.

f) Clad piping for subsea service – fabrication

In the production of large-diameter clad pipe from clad plate, the clad side of the longitudinal weld can be completed by normal back cladding techniques using an internal boom. For girth welds and longitudinal welds in smaller diameter pipe, single side welding techniques are necessary.

There are two basic techniques for single side welding of

clad pipe which can form the basis of detailed weld procedures:

a) Using high alloy consumables for the complete joint.

b) Welding the clad layer first with a GTAW root and reinforcing pass. A buffer layer of very low carbon iron is next deposited and then the joint is completed with appropriate carbon steel electrodes.

Weld overlaying is being used extensively for subsea system components, e.g. valves, sphere tees in an Alloy 625 riser system, external corrosion protection of pipe penetrations into concrete structures, etc. *Reference* 33 describes a particular application in the shore approach tunnel for the Oseberg transportation pipeline.

MISCELLANEOUS APPLICATIONS

a) Splash zone sheathing of risers

Experience[36] has shown that concrete cladding of hot risers can be dangerous. The splash zone cladding is prone to physical damage from floating objects and highly oxygenated seawater on the hot metal surface can cause catastrophic corrosion. Serious incidents have occurred in the Arabian Gulf and in the North Sea[36] resulting in extensive fire damage and in one case well loss.

Splash zones can be protected using metal sheathing – 3-4mm-thick Alloy 400 (70/30 nickel-copper) has been extensively used for this purpose. Attachment methods for sheathing were reviewed by McKeown[37].

A recent development has been the use of 90/10 cupronickel for sheathing applications.[38]

b) Pump columns

Vertical lift pumps are commonly used to deliver seawater to the platform. The casing and impeller are located below the low tide level at the end of a series of vertical column pipes which are fastened to the jacket. These column pipes are essentially part of the piping system.

Alloy materials commonly used for these pipes are Ni-Resist cast iron (the D-2 grade is widely used) and nickel aluminum bronze (both wrought and cast grades).

Ni-Resist is anodic to stainless steels and provides cathode protection which is particularly useful during shutdown periods. Pumps often use Type 316 stainless steel for the shafting with the cast equivalent (CF-3M or CF-8M) for the impeller. During operation, the high resistance of the stainless steel to fast-flowing seawater is beneficial and pitting is not a problem during shutdowns.

Ni-Resist irons for use in warm seawater should be stress relieved (1 hour at 650°C followed by cooling) to minimize the risk of stress corrosion cracking.

Nickel aluminum bronze has been used for pump colums, particularly where the same alloy is used for pump casing and impeller. This alloy has good resistance to fast-flowing seawater in both cast and wrought form. Care is needed, however, where column pipes are fabricated from plate with a seam weld. The alloy is prone to dealuminification at the heat affected zone in seawater and the dealuminified zone

has poor mechanical properties. A pressure surge can cause sudden failure through this layer.

Centricast piping with welded-on flanges are at less risk as the stresses on the circumferential weld is about half that of the longitudinal seam weld described above. Heat treatment –4-8 hours at 675°C–will reduce the tendency to dealuminification and is beneficial. However, the susceptibility can only be removed by a high-temperature treatment which is not feasible on finished fabrications.

Where all-stainless steel pumps are used, as for example in stainless steel seawater systems, then alloys with high resistance to pitting and crevice corrosion should be used, i.e. alloys with PRE_N greater than 40.

c) Expansion bellows

The use of expansion bellows of multiply alloy construction to compensate for expansion or contraction in piping systems operating at elevated temperatures or subzero temperatures respectively is well established practice in all sectors of process industry and platform topside process piping is no exception. A typical example on offshore platforms would be gas turbine exhaust systems.

The 300 series austenitic stainless steels, e.g. Type 316L, 304L, have long been important materials for expansion bellows. However, their susceptibilility to chloride stress corrosion cracking at elevated temperatures when handling chloride-containing fluids or operating in a salt-laden atmosphere has lead to the widespread use of high-nickel alloys (nickel having the property of increasing resistance to chloride stress corrosion cracking)[39] for this application, princially Alloy 825 or Alloy 625. In Europe bellows manufacturers have tended to specify mainly 825 for standard products although Alloys 625 and 400 find some usage whereas their US counterparts have generally opted for Alloy 625.
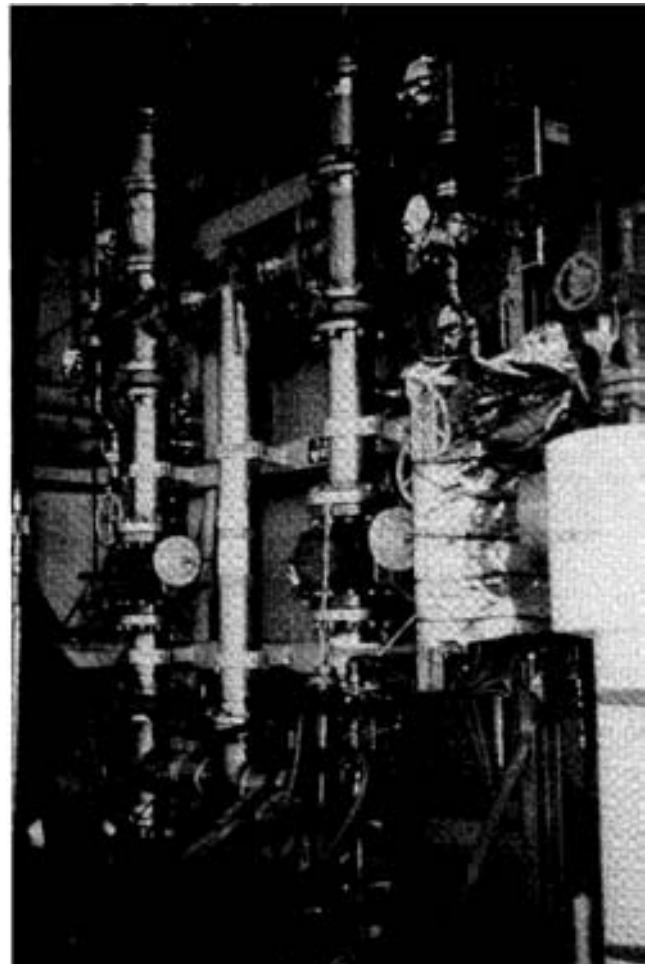
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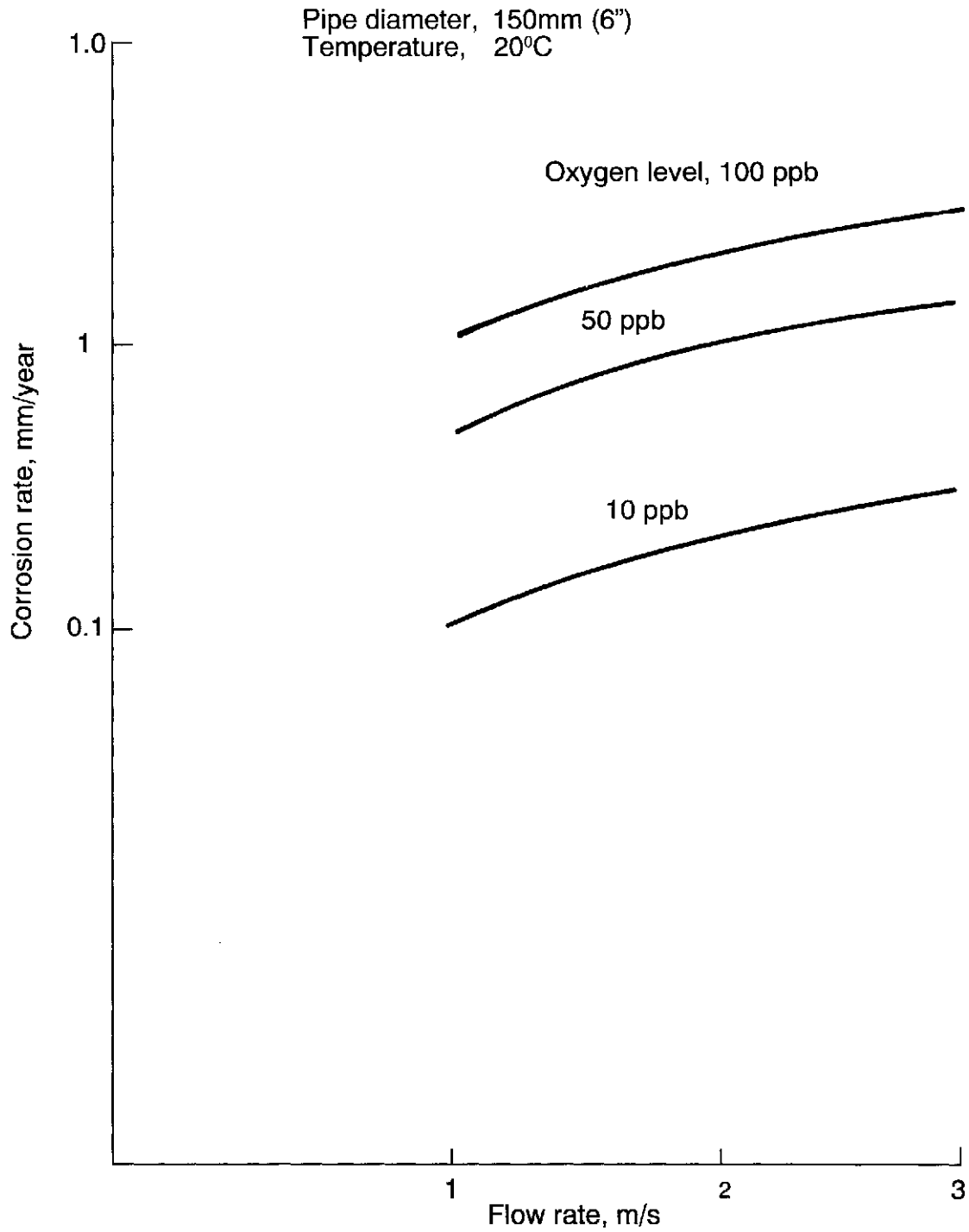
Figure 1   90/10 Copper-nickel alloy piping to be used in seawater hyperfilters.

Figure 2   Avesta 254 SMO piping in the firefighting system on Gullfaks A.

Figure 3

Pipe diameter, 150mm (6")
Temperature, 20⁰C

Oxygen level, 100 ppb

50 ppb

10 ppb

Corrosion rate, mm/year

1.0

1

0.1

Flow rate, m/s

1   2   3

Estimates of corrosion of carbon steel in seawater as a function of flow rate at various oxygen concentrations.

Figure 4
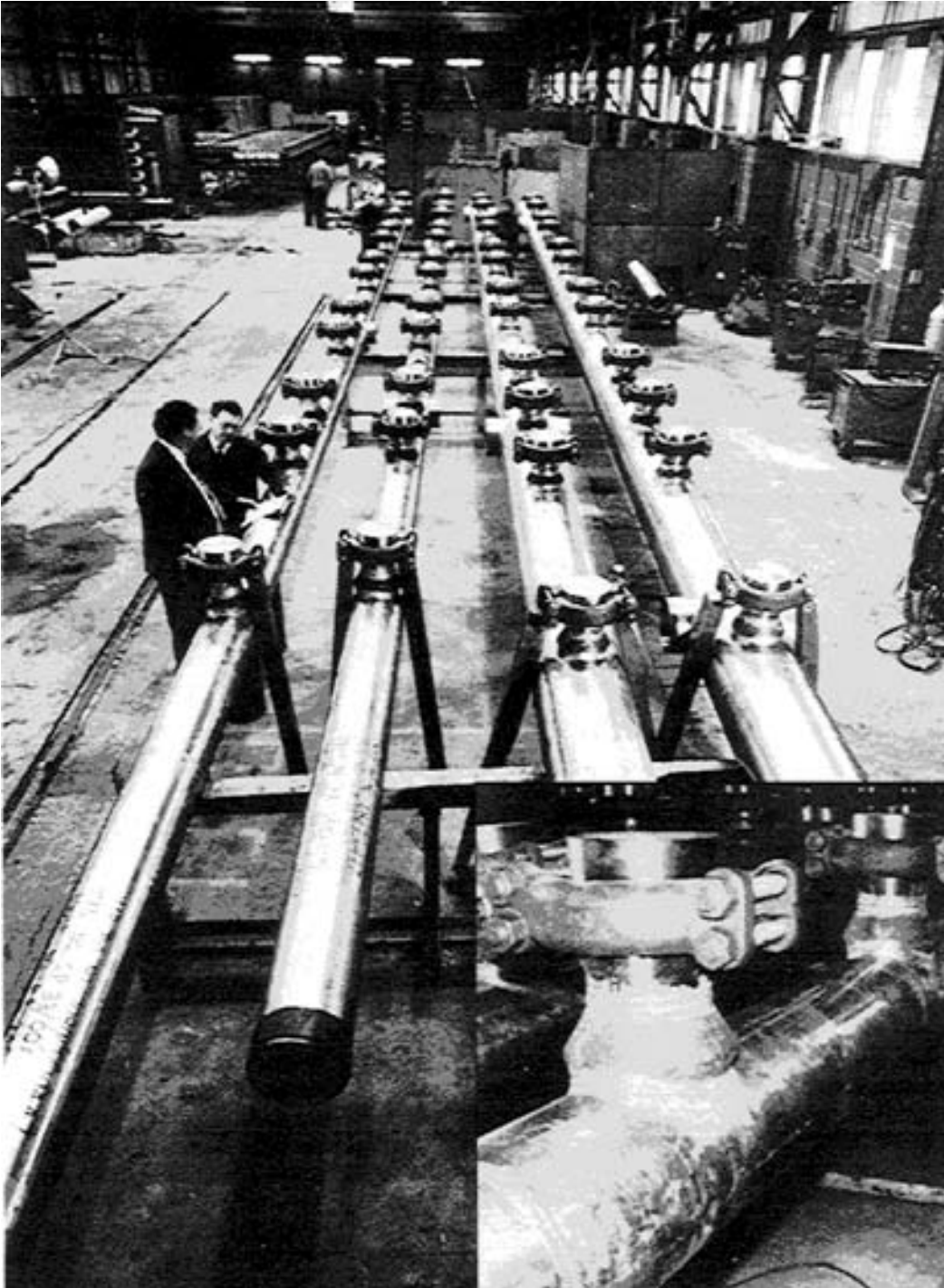
*Courtesy Marathon Oil (U.K.) and Scomark Engineering.*

Alloy 825 production and test manifolds for a North Sea platform – the run pipe is centrispun.

Figure 5a H_2S limits for avoidance of SSCC of duplex stainless steel UNS 31803
Slow strain rate test results for duplex stainless steels
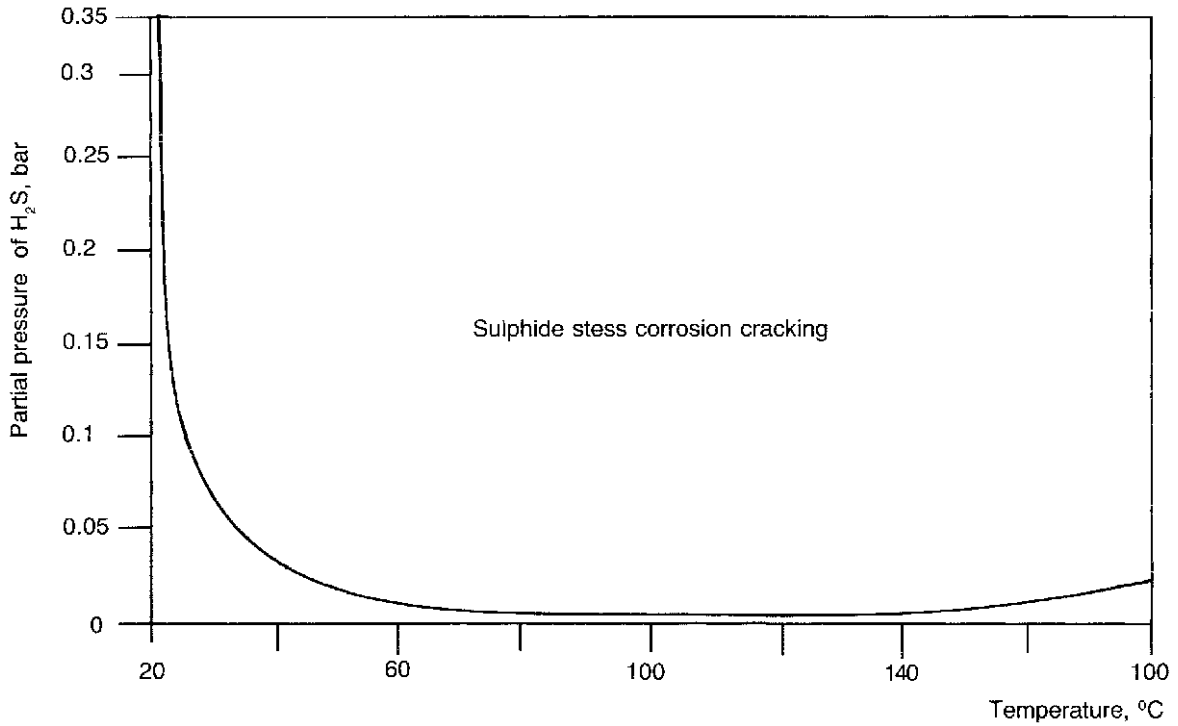
Figure 5b

High pressure SCC tests of 50% cold-worked tubes of SAF 2205 in 5% and 15% NaCl with a partial pressure of CO_2 equal to 70 bar (1000 psi) at temperatures between RT and 260°C (500°F).
Stress = R_pO_2 at testing temperature. Testing time 500h. Partial pressure of H_2 S, bar –1 bar = 100 kPa.
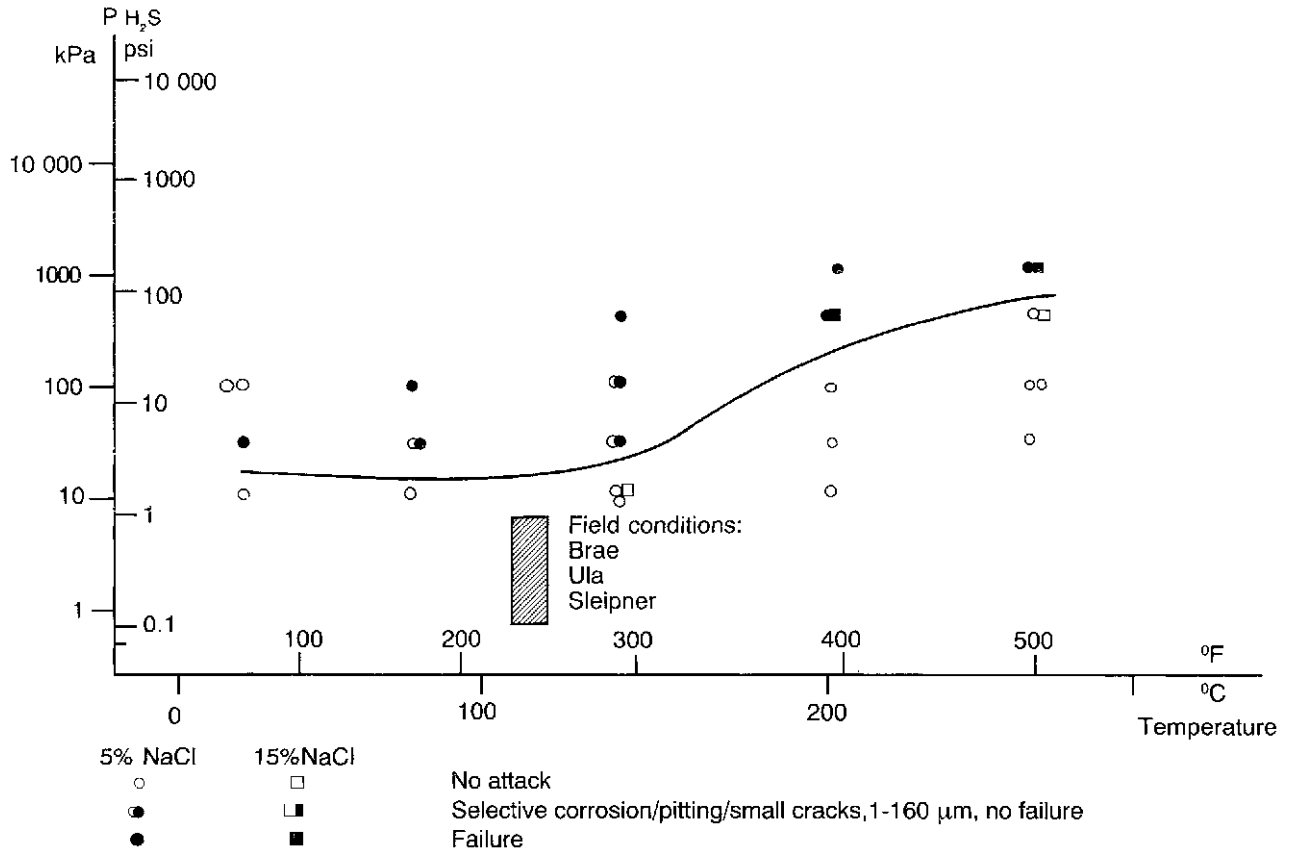
Figure 6
Economic evaluation of stainless steel vs carbon steel pipelines.
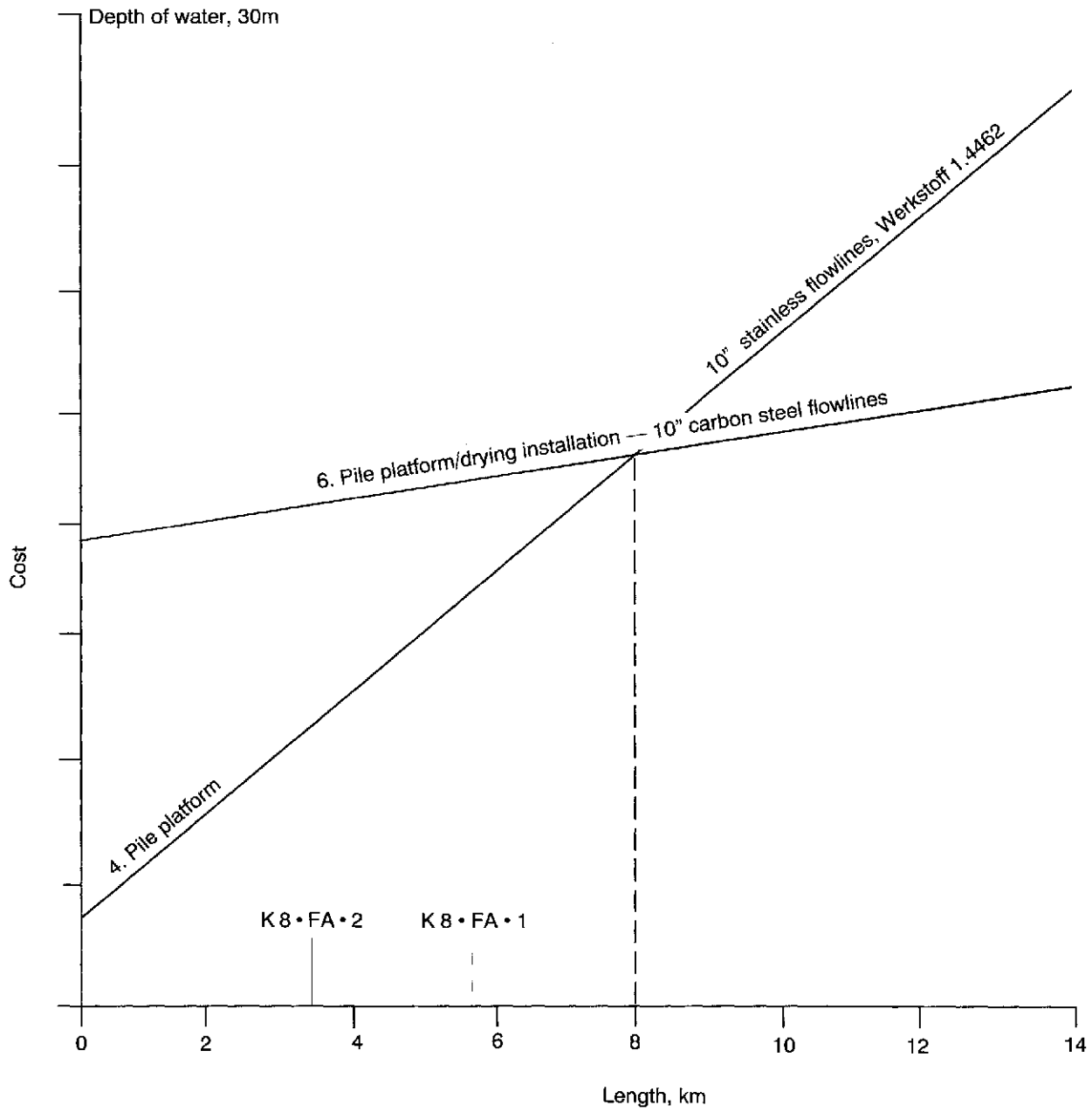
Figure 7

Welding of Sean/Indefatigable duplex stainless steel lines.

Figure 8

Price comparision of bimetalic to solid pipe, in April 1986

1. Material : Solid pipe: KCR42N (cast Alloy 825)
   Bimetal pipe: Outer pipe: API 5L X65
                  Liner: KCR42N (cast Alloy 825)

2. Unit length: 12m

Solid pipe

o Sch. 80
• Sch. 120
□ Sch. 160

Bimetal

o Sch. 80
• Sch. 120
□ Sch. 160

Price
index

Outside diameter
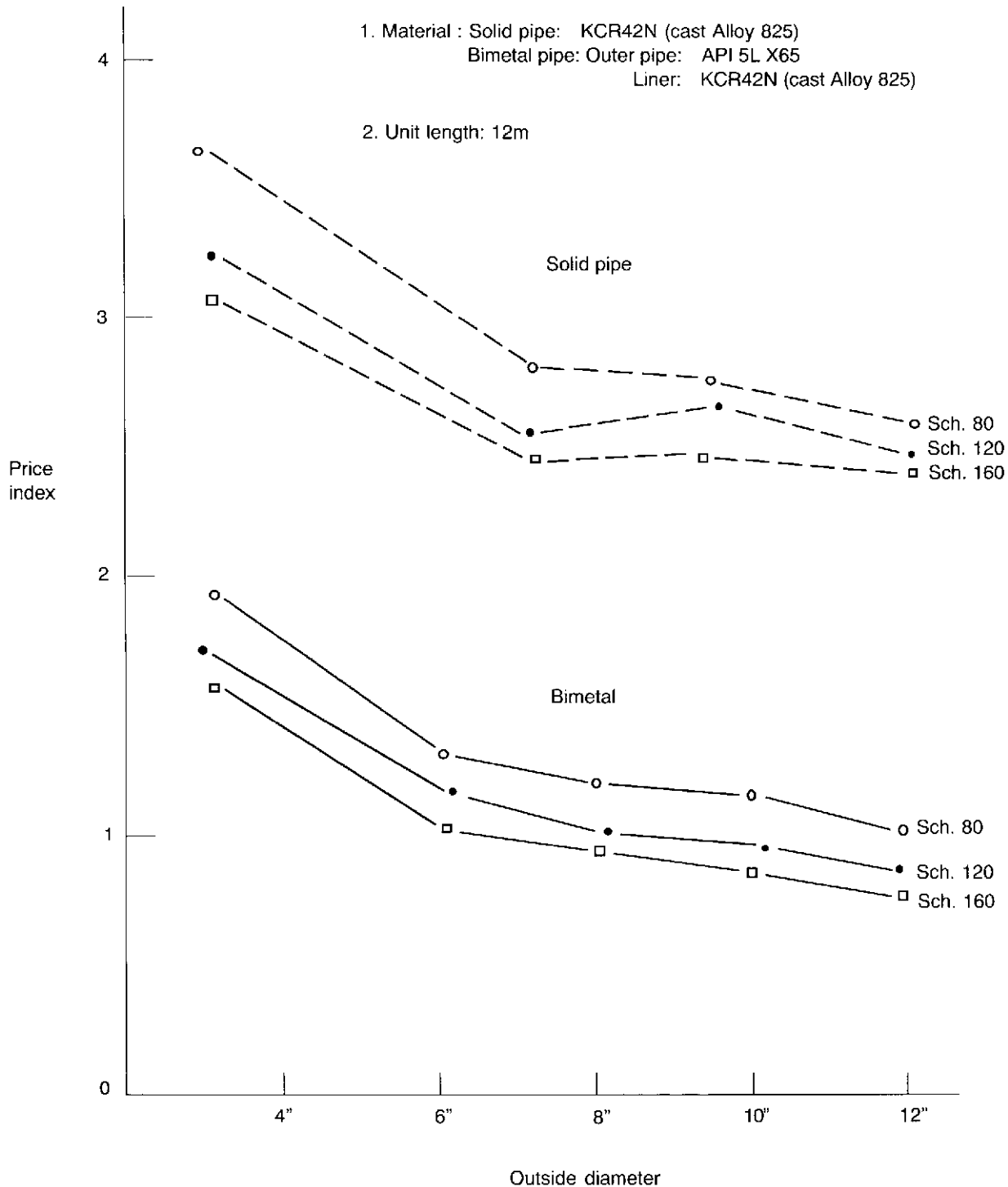
Table 6   Offshore applications of internally-clad steel pipe

	Location	Field	Application	Material	Length	Remarks
1	Southern North Sea	Gas	3 x 12" clad risers	X-60 pipe clad with 3mm Alloy 625 Sphere tees &flanges weld overlaid with Alloy 625		These risers were not amenable to pig monitoring and inhibition not provided.
2	Southern North Sea	Gas	8" clad flowlines	X-60 clad pipe with 3mm 316L	9 miles	
3	North Sea	Oil	30" clad risers	X-60 clad with 3mm 316L		
4	North Sea	Oil	Subseamanifold piping on 36m x 18m x 10m template	Centrifugally-Cast X52 pipe with 3mm Alloy 625	≃ 1000m clad pipe	Manifold tees from solid Alloy 625. Weld neck flanges weld overlaid with Alloy 635. Under construction 1988.
5	Indian Ocean	South Bassein gasfield	2 subsea lines	X65 Pipe with 3mm Alloy 825 cladding	1 x 24" line, 6.5km 1 x 20" line, 4.4km	Line handles 6-8% CO_2 0.12% H_2S with chloride-containing water. Under construction 1988.

Appendix: Composition and properties of alloys referred to in text
(a) Copper base alloys

	UNS N°	Copper	Nominal composition				Mechanical composition	
			Aluminum	Nickel	Iron	Manganese	0.2% Proof min N/mm^2	UTS min N/mm^2
90/10 Copper nickel	C70600	Remainder	-	10	1.5	1	103*	275
Nickel aluminum bronze, cast alloy	C95800	Remainder	9.5	5.0	5.0	1.5	240+	585+
Nickel alumunum bronze, wrought alloy	C63000	Remainder	10	5	5		235*	620*

* ASTM B171 (converted from ksi)   +ASTM B148

(b) Standard and special austentitic steels

	UNS N°	PRE$_N$	Nominal composition							Mechanical properties	
			C	Cr	Ni	Mo	Cu	N	Other	0.2 Proof min N/mm^2	UTS Min N/mm^2
316L	S31603	25	.03	17	12	2.5				170	485
254SMO	S31254	43.0	.03	20	18	6	0.8	0.2		300	650
6XN	N08367	45.6	.03	21	25	6.5	-	0.2		317	718
1925 HMO	N08095	43.2	.03	21	25	6.0		0.15		300	600
904L	N08904	35	.03	20	25	4.5	1.5	-		220	520
Alloy 28	N08028	38	.02	27	31	3.5				220	490

(c) Duplex stainless steels

Type	UNS N°	PRN$_N$	Nominal composition							Mechanical properties	
			C	Cr	Ni	Mo	Cu	N	Other	0.2 Proof min N/mm^2	UTS min N/mm^2
22% Cr (22/5/3/N)	S31803	34	.03 max	22	5.5	3.0	-	0.14		450	680
25% Cr (25/6/3/N)	S32550	≏ 38	.04 max	26	5.5	3.0	1.5-2.5	0.15		550	760
Proprietary alloys											
Zeron 100	-	≥40	0.03 max	25.0	7.5	3.8	0.7	0.25	W 0.7	550	750
SAF 2507	-	≥40	0.03 max	25.0	7.0	4.0		0.25		550	800
Fermanel	-	≥40	0.06 max	27.0	8.5	3.0	1.0	0.25		420	700
Uranus 47N	-	≥38	0.03	25.0	6	3.0	<0.5	0.20		500	700

(d) Medium- and high-nickel alloys

	UNS N°	PRE$_N$	C max	Cr	Ni	Mo	Cu	N	Other	0.2% Proof min N/mm^2	UTS min N/mm^2
					Nominal composion						**Mechanical properties***	
Alloy 400	N04400	-		-	63 min	-	31	-	Fe 2.5 max	195	480
Alloy 825	N08825	31	.05	21	42	3.0	2.25	-		241	586
Alloy 625	N06625	>50	0.1	21.5	58 min	9.0	-	-	Nb 3.6	414	827
AlloyC276	N10276	>60	0.01	15.5	Bal	16			Fe 4/7 W 3.75	283	690