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SPECIAL REPORT

OFFSHORE '88



High performance alloys: How they are used offshore

Increased safety, reduced equipment weight and less maintenance are a few advantages of stainless steels and nickel-based alloys. And as water depths increase and wells become more critical their use will intensify

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Editor's note:

Last January, The Nickel Development Institute, Toronto, sponsored a one-day seminar exclusively for the oil and gas industry. Held in Houston, it drew attendance from all the major oil companies and their research centers in the U.S. and Canada. The purpose was to provide a forum for discussion of material applications and corrosion problems, and to provide an update of the latest developments and experience with corrosion-resistant alloys. At popular request NiDI is considering repeating this on an annual basis. C. M. Schillmoller, chairman of the seminar, provides a few highlights on information that was presented.

STAINLESS STEELS and nickel-based alloys are increasingly applied in the oil and gas industry for exploitation of sour crudes. Containing considerable quantities of H₂S, CO₂ and salted formation waters, these crudes show a high corrosivity with respect to general corrosion and stress corrosion cracking by sulfides (SSCC), by chlorides (CSCC) or

by their combined action. Traditionally Monel, K-Monel and copper-nickel alloys have served the industry well for sucker rods, instrumentation, packers, valves for gas lift, pumpshafts, sea water piping, heat exchange tubing and many other critical components.

In the new generation of offshore platforms, deep sour gas wells, CO₂ enhanced oil recovery projects and production in the Arctic, extensive use is now being made of the specialty Cr-Ni-Mo stainless steels and the Ni-Cr-Mo alloys for extremely severe corrosive applications. Examples of applications will be cited, an economic analysis provided of using the corrosion resistant alloys (CRA) in downhole tubulars and several suggestions for reducing the weight of topside construction on offshore platforms. Further, guidelines will be presented for the selection of alloys to reliably resist the very aggressive corrosive environments.

Offshore applications

The search for oil beneath the seabed and its subsequent development has increased significantly during recent years. Offshore activities account for close to half of the new reserves, found, and about a quarter of world oil production—some 15 million bpd.

Protection of steel. The jacket of a large multi-well platform may require as much as 6,000 t of structural steel. To protect the steel a good coating system is applied prior to installation, augmented by cathodic protection. Severe corrosion has been experienced in the splash zone and riser pipes as well as fatigue failures in the welded tubular joints. A cast-nodes design, using a 2.5% Ni-Cr-Mn steel composition can substantially reduce stress concentrations in the welded joints.

Monel alloy 400 (UNS N04400) sheathing of piling in the splash zone of the structure has been applied for over 40 years initially in the Gulf of Mexico, and later adopted worldwide because of its good performance. Presently a

TABLE 1—Weight comparison of stainless steel versus copper-nickel for two typical seawater piping systems on an offshore platform

Design velocity: SS 20 ft/sec CuNi 7 ft/sec	Avesta 254 SMO Stainless steel			90-10 CuNi Cupronickel		
	Size, in.	Wall thickness, mm	Weight, Tons	Size, in.	Wall thickness mm	Weight Tons
1) Seawater lift discharge from pumps: 6m pipe + 3 flanges and 1 valve per pump	14	4.78	2.7 (dry)	20	7.5	5.8 (dry)
	14	4.78	5.5 (wet)	20	7.5	11.5 (wet)
2) Seawater lift header 180m straight pipe	26	6.35	18.7 (dry)	36	8	37.7 (dry)
	26	6.35	77.9 (wet)	36	8	151.7 (wet)

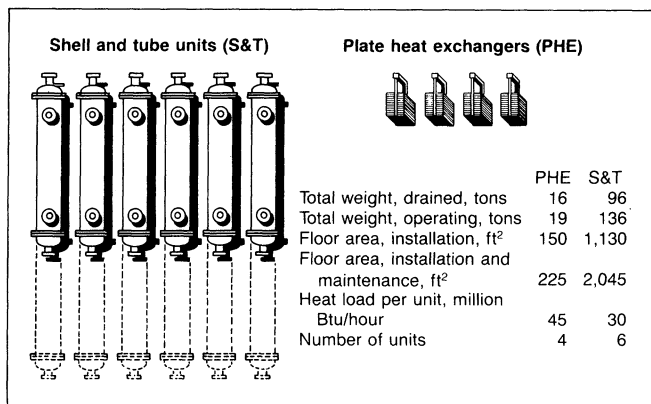


Fig. 1—High performance alloys allow plate type heat exchangers to replace tube and shell types thereby significantly reducing weight and space requirements in an offshore application.

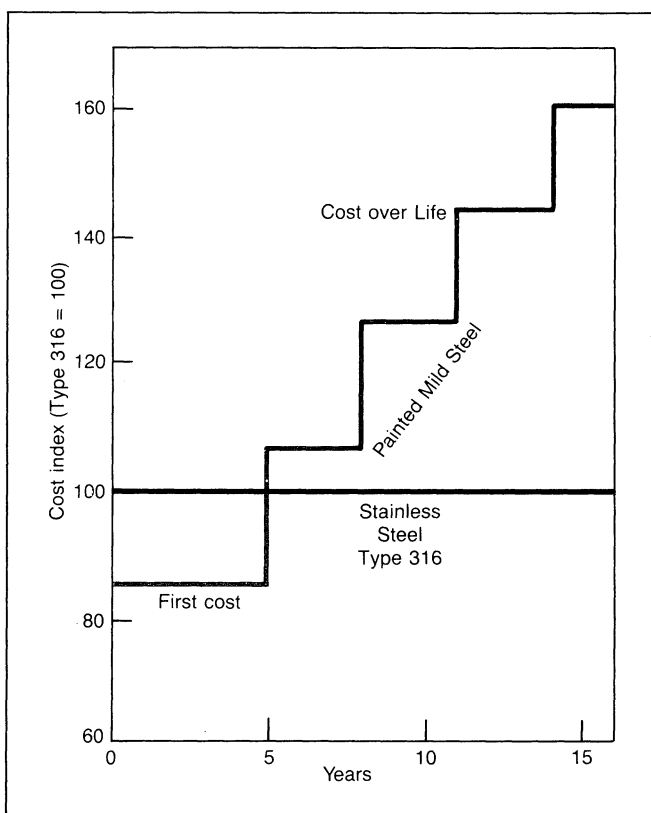


Fig. 2—Although initially more expensive, stainless steel used in platform topside components saves money later because of its lower maintenance needs.

number of companies are considering 90-10 Cu-Ni sheathing to substantially reduce biofouling and reduce wave-loading on the structure. Thick cement coatings have been used on hot risers, but they lack reliability. Failures have resulted in serious fire damage and production loss. It is now common practice to sheath risers with Monel alloy 400, Inconel alloy 625 (UNS N06625) or similar materials.

Seawater systems. Offshore production and processing platforms use large amounts of seawater for firefighting and cooling purposes, and for water injection to enhance oil recovery. These systems involve large weights of material for piping, pumps, valves and heat exchangers. Following ship-board experience, 90-10 cupronickel (UNS C70600) has been used for many years, especially in the North Sea and Brazil.

Most designers allow 6 to 8 fps design velocity for copper-nickel. Except for short sections following the pumps, where

high velocity and turbulence occur, it has performed very well. Cu-Ni has a life expectancy of 20 years compared to 6 to 9 years for coated and galvanized steel. Monel alloy 400 can be used in sections where impingement and higher velocities are encountered. Copper-base alloys also suffer corrosion in seawater containing sulfides, for example, piping leading to storage cells in the base alternately filled with oil and seawater ballast.

This has led to considering stainless steel for piping. Any of the 6% Mo specialty stainless steels are suitable for this application. Avesta's 254SMO (UNS S31254), a 20Cr/18Ni/6Mo stainless steel, has been used extensively on Norwegian platforms. Keen interest was shown in this development by other operators and now more than 30 thousand t of alloy has been supplied over the past three years for piping. A major reason for this is that it can withstand a much higher flowrate than copper-nickel and is twice as strong. Therefore one can design in a smaller diameter, and thinner wall. As a result one ends up saving 50% on piping weight and 35% on installed piping cost. The biggest gain, however, is in being able to save 50 to 60% in wet weight when the pipes are filled with seawater. Table 1 shows a weight comparison. The economic value is in reducing topside weight. Shell Oil has published figures indicating that removing one ton in top weight will allow the supporting structure to be reduced by three t, and thereby save about \$150,000.

Process systems. Sandvik's Sanicro 28 (UNS N08028), INCO's Incoloy 825 (UNS N08825) and VDM's 904hMo (UNS N08925) are popular choices for process piping since they generally handle the full range of H₂S/CO₂/oil/gas/brine compositions that may be encountered. Also these alloys are highly resistant to chloride stress cracking and sulfide stress cracking. Frequently, plate type heat exchangers are preferred over the tube-and-shell since they are very compact in size and again their dry, as well as wet, weight is substantially less than the standard tube-and-shell variety as shown in Fig. 1.

Initially, titanium plates are invariably selected, because they are very thin, light and the herringbone pattern and counterflow give good heat transfer. A number of offshore platform operators have reported crevice corrosion on the titanium plates where in contact with the gaskets and they have switched to a 6Mo specialty stainless or Alloy 625. Other applications for Alloy 625 are: expansion bellows for decklines and steam pipelines and for the boom of the flare stack and flare tip.

New generation developments. One is starting to encounter clusters of offshore platforms used for drilling and feeding wet oil/gas mixtures to a central production platform for oil/gas/water separation. The gas is dried before pumping it by pipeline to the coast. In the North Sea where substantial quantities of CO₂ make the wet gas very corrosive, it was economically justified to use 2205 duplex stainless steel piping, rather than place separation/drying facilities on each platform. When substantial quantities of H₂S (over 10 psi partial pressure) are present in the gas then Alloy 825 or Alloy 625 clad-steel piping should be considered.

For a large installation off the Indian Coast, Alloy 825

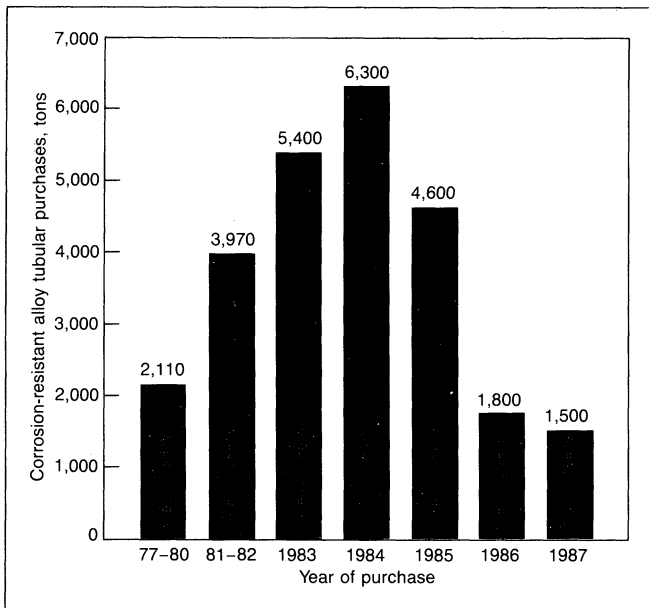


Fig. 3—Purchases of corrosion-resistant alloys in the U.S. peaked in 1984, but there is optimism that sales will begin to pick up as operators continue development of high pressure sour gas offshore as well as deep, hot wells onshore.

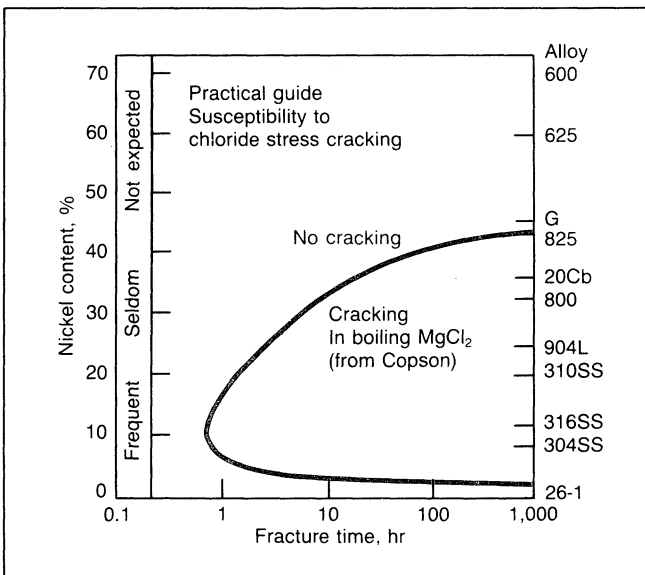


Fig. 4—Chart shows the influence of nickel on chloride stress corrosion cracking of alloys.

clad-steel has been specified.

Subsea completions are used as an alternate to drilling platforms especially in the deeper waters. Some of these use flexible pipe, which with its stainless steel armor and reinforcements is well suited for deep sea work. They are frequently bundled, comprising product lines and hydraulic/electrical umbilicals. Both 316L and duplex 2205 stainless steels have been used in this application. The pipe is flexible and can be wound onto drums in continuous lengths up to 5,000 ft. The duplex stainless offers higher fatigue strength and superior pitting and crevice corrosion, and can be designed in lighter wall than 316L stainless.

Topside equipment. The main deck is made of high strength steels to reduce weight. Stainless is not used structurally but for cladding and other non-weight bearing applications. Examples are external and internal cladding of living quarter modules, for ventilation louvers, instrumentation and pneumatic pipework, cable ladders, cable trays, outside stairs of crew quarters, fire doors, grating and in some cases, helidecks. Type 316 is used for its weather resistant properties, requiring no maintenance. British Steel Corp. reported the use of approximately 2,000 tons per year of stainless steel for offshore platforms in the North Sea for these applications. Fig. 2 shows the justification against painted mild steel, which over a 20-year life span costs substantially more. Safety and fire resistance in addition to low maintenance are strong arguments in favor of using corrosion resistant alloys. Prefabrication of the various modules on-shore reduces weight, gives better quality and improves delivery time. The units are tugged out and lifted into place.

Natural gas production

The fundamental supply/demand forces for energy in the U.S. and around the world assure a strong growth in natural gas over the next five years. New major gas markets are: firstly the power industry, secondly for steam floods in California to develop heavy crudes, and thirdly as a substitution for oil to reduce U.S. dependency on oil imports, which will be approaching 50% in the early 1990s and will contribute at that time to at least \$75 billion of our import/export deficit.

Deep sour gas. After coal, natural gas is the most bountiful energy source in the country, and all it takes is removal of regulatory barriers to satisfy demand. A repeat of the period 1977-1983, when 10,000 to 15,000 new gas wells were drilled each year, would mean a strong increase in reserves and many new long-term gas supply contracts. Many of those wells were deep sour gas wells, 20,000 feet or deeper, with high concentrations of H_2S and CO_2 in formations containing pressures of 10,000 to 20,000 psi and bottomhole temperatures greater than 400°F. H_2S concentrations over 28% and CO_2 concentrations of 3% to 10% have been encountered.

New technology. New metallurgy was developed and technology was established to use corrosion resistant alloys (CRA) to eliminate troublesome inhibition systems, obtain better well design, lengthen well life and increase well productivity. Over the past 10 years over 25,000 t of corrosion-resistant tubulars have been installed. Fig. 3 shows the quantities and year of purchase. For obvious reasons a slowdown has taken place since 1985.

Presently there is new optimism as Mobil Oil begins production from its lucrative Mary Ann field in Mobile Bay, Ala. Exxon also has made discoveries in the prolific Jurassic Norphlet deep gas trend off Alabama in the Gulf of Mexico. The project eventually could produce as much as 600 MMcf/d of gas from 27 wells. A number of these wells and the four by Mobil have been completed with Hastelloy C-276 tubulars.

Alloy selection. How does one select the optimum alloy for tubulars to withstand 11% H_2S and 5% CO_2 for a string 21,500 feet deep and pressures in excess of 10,000 psi and temperatures of 425°F? Autoclave tests performed by Exxon

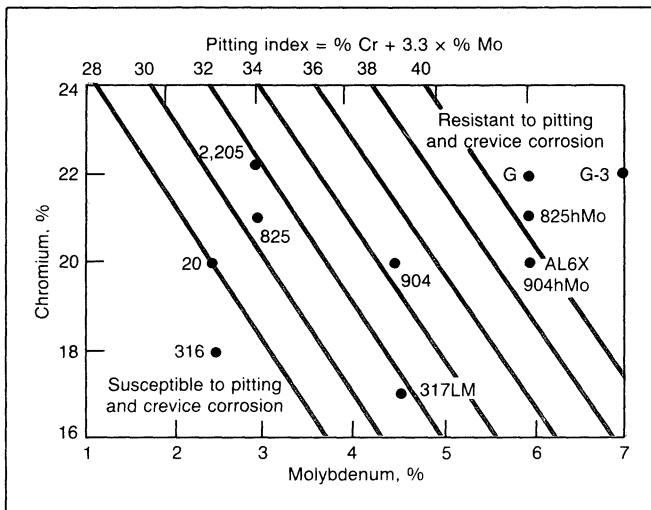


Fig. 5—Influence of chromium and molybdenum content on pitting and crevice corrosion of alloys.

and Mobil's research laboratories attempted to duplicate downhole conditions by adding to the test environment 25 weight percent NaCl and, in the case of high H₂S partial pressures, by adding some elemental sulfur (1 g/L). Under extremely severe conditions, because of the risk factor, one sometimes tends to over specify. Hastelloy C-276 has been found to perform very well when the interaction takes place among wet CO₂ (carbonic acid formation, low pH), wet H₂S (general corrosion and sulfide stress cracking), produced chlorides (chloride stress corrosion cracking, severe pitting under acid conditions) and free sulfur (acts as an oxidizer and accelerates pitting attack). A summary of the corrodents and their interaction is shown in Table 2.

TABLE 2—Corrodents and their interactions

System	Corrodent	pH	Mode of attack
Sweet	Wet CO ₂	3.0 to 6.0	General acid corrosion
Sour	Wet H ₂ S	> 6.0	SSCC, general corrosion
Brines	Chlorides	> 6.0	CSCC, pitting, general
H ₂ S/CO ₂ /Brines	Chlorides	3.0 to 6.0	SSCC, CSCC, pitting, general
H ₂ S/CO ₂ /Cl ₂ /S	Oxidizer	3.0 to 6.0	SSCC, CSCC, pitting accelerated

Sweet is less than 1 ppm H₂S (0.05 psi), sour is above 1 ppm H₂S, aerated is over 10 ppb oxygen, free sulfur acts as oxidizer, high pH is over 6.0, low pH is between 3.0 and 6.0

TABLE 3—Typical high-alloy materials being considered for corrosive oil field service

Type	Materials	Composition, %								
		Fe	Ni	Cr	Mo	Cb + Ta	Ti	Al	Cu	Others
Stainless steels	Martensitic	12 to 13% Cr	bal	—	12	—	—	—	—	—
		CA6NM	bal	4	12	0.70	—	—	—	—
Precipitation hardened	17-4 pH (martensitic)	bal	4	17	—	—	—	—	4	—
	Custom 450 ² (martensitic)	bal	6	15	0.75	—	—	—	1.5	—
Austenitic	A-286 (austenitic)	bal	26	15	1.3	—	2.0	0.2	—	0.015 B
	20Cb-3 ²	bal	33	20	2.5	1.0 max	—	—	—	—
	904 L ⁷	bal	25	20	4.5	—	—	—	1.5	—
	AL 6X ⁹	bal	24	20	6.0	—	—	—	—	—
Duplex (austenitic/ferritic)	Sanicro 28 ³	bal	31	27	3.5	—	—	—	1.0	—
	AF-22 ⁴ /SAF-2205 ³	bal	5.5	22	3	—	—	—	—	0.14N
Nickel alloys	Uranus 50	bal	7	21	2.5	—	—	—	1.5	—
	Ferrallium ⁵ 255	bal	5.5	26	3	—	—	—	3	0.1 N min
	DP-3 ⁸	bal	6	25	1.5	—	—	—	—	0.1 N min
Cold reduced	Hastelloy C-276 ⁵	6	bal	15	16	—	—	—	—	2.5 Co max, 4.0W
	Hastelloy G ⁵	20	bal	22	6	2	—	—	2.0	2.5 Co max, —
	SM2550 ⁹	bal	50	25	6	—	—	—	—	—
	Inconel 625 ⁶	5	bal	21	9	3.5	0.2	0.2	—	—
	Incoloy 825 ⁶	30	42	22	3	—	0.9	—	2.25	—
	Incoloy 800 ⁶	45	32	21	—	—	0.4	0.4	0.38	—
	Inconel 718 ⁶	19	bal	19	3	5.0	0.9	0.5	0.15	—
	Pyromet 31 ²	15	bal	23	2	0.85	2.3	—	1.3	0.005 B

1. Armco Inc. 2. Carpenter Technology Corp. 3. Sandvik Inc. 4. Mannesmann AG 5. Haynes International 6. Huntington Alloys Inc. 7. Nyby Uddeholm AB 8. Sumitomo Metal Ind. Ltd. 9. Tech Specialty Metals

Factors in alloy selection

During the past ten years there has been an increased use of stainless steels and specialty alloys containing high levels of chromium, nickel and molybdenum. A typical selection of high-alloy materials for sour oil field service is listed in Table 3. Since degradation can take the form of general corrosion, chloride stress corrosion cracking, sulfide stress corrosion cracking or pitting and crevice corrosion, all these modes of corrosion have to be considered when selecting an alloy. This is especially so, since in the majority of failures, corrosive attack occurs rapidly and is of a localized nature.

Intergranular corrosion. This is chiefly associated with stress in the heat-affected zone adjacent to welds, and can be readily controlled by using stainless steels with a low carbon content (0.03% C max), or stabilizing the alloy with Ti or Cb to avoid harmful precipitation.

Chloride stress cracking. Types 304 and 316 stainless steels are very susceptible to CSCC. While tests in boiling magnesium chloride have shown that alloys with 42% Ni and over are fully resistant to CSCC, a more practical rule is that alloys with a minimum nickel content of 22% seldom experience CSCC. Fig. 4 shows the fracture time in boiling MgCl₂. It shows alloys such as 825, G, 625 and C-276 as fully resistant, and alloys such as 904, 28 and 20 that seldom experience CSCC. In addition to the nickel-base alloys, ferritic stainless steels and stainless steels with a duplex ferritic-

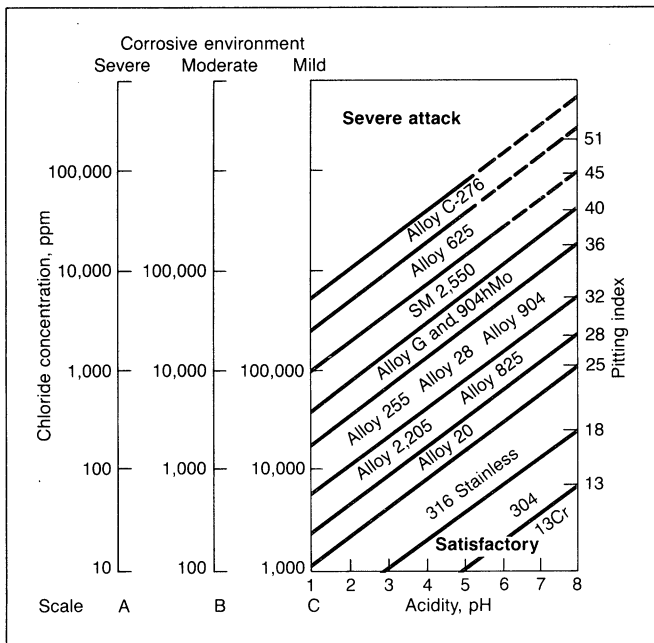


Fig. 6—Susceptibility of various alloys to pitting and crevice corrosion in an acid brine media.

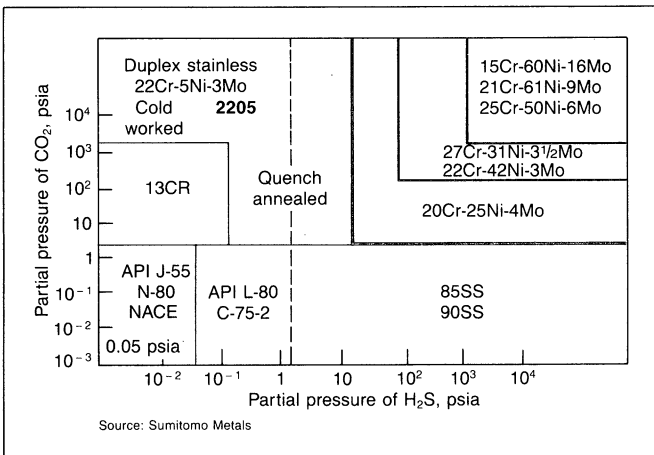


Fig. 7—Selection guide for tubulars in sweet and sour wells. Used in combination with Fig. 6, this chart will help assure proper tubular selection.

TABLE 4—Incremental* costs (present value) of comparative corrosion alleviation systems, five-well offshore sour gas field

	Low alloy system	Mixed alloy system	CRA system
Tubing and Christmas tree	-0-	\$15,000,000	\$15,000,000
Flowline base	-0-	-0-	3,000,000
Inhibitor treatment facilities	\$2,000,000	1,500,000	-0-
Platform space for inhibitor treatment facilities	20,000,000	10,000,000	-0-
Inhibition annual operating expense	2,700,000	1,350,000	-0-
Cumulative operating expense	21,000,000	10,500,000	-0-
Total cost	\$51,700,000	\$38,350,000	\$18,000,000

* Base case low alloy steel, 20 year life, 12% deferment factor.

austenitic structure are highly resistant to CSCC. Alloys such as 2205 and 255 did not stress crack when tested in boiling seawater, and have given an excellent account of themselves in industry.

Pitting and crevice corrosion. The resistance of alloys to pitting and crevice corrosion is enhanced by the addition of chromium and molybdenum. In ranking alloys as to pitting resistance, an empirical formula, adding $\frac{\%Cr}{3.3} + \frac{\%Mo}{16}$ content, is frequently used. In the case of duplex stainless steels one also adds $16 \times$ the nitrogen content. The higher this so-called "Pitting Index" the more resistant the alloy. Fig. 5 shows the pitting index for a number of alloys. As can be readily appreciated, other alloys that may be of interest to the user can be added easily. Each environment has a critical index number.

For example, in the case of seawater with a chloride content of 20,000 ppm and a pH of 7.8, we find that alloys with an index of 32 and above are resistant to pitting, while those with an index of 36 and above are resistant to crevice corrosion. The pH, chloride concentration, presence of oxygen or oxidizers and the temperature are the predominating controlling factors. Design is always based on crevice corrosion resistance.

Fig. 6 was developed to predict the usefulness of various alloys in the petroleum industry, showing pH versus chloride concentration. Please note that there are three vertical scales. Scale A, marked as *Severe corrosion*, depicts the presence of oxygen or free sulfur in the systems with operating temperatures in the 175°C to 260°C range and with high partial pressures of H₂S and CO₂. One may assume that this scale would apply to deep wells such as Mobile Bay. Scale B, *Moderate corrosion*, has no oxygen or free sulfur present, moderate to high partial pressures of H₂S and CO₂ and temperatures in the range of 110°C to 200°C. One may assume that this scale would apply to many of the deep wells and offshore operations. Scale C, *Mild corrosion*, has no oxygen in the system and would cover many of the high CO₂ wells with low H₂S partial pressure and at moderate temperatures.

Sulfide stress cracking. With the increasing trend toward mitigating corrosion and obtaining high strength with stainless steels and nickel alloys, there has been much interest in the corrosion and embrittlement behavior of these alloys in H₂S/sulfur-containing brines.

Even though SSCC is a low-temperature phenomenon (below 60°C), environmentally-induced stress cracking has been identified on high alloy materials at elevated temperatures. NACE Standard MR-01-75 in its recent revision recognizes certain strength and hardness limitations for the corrosion-resisting alloys.

Please note that the susceptibility of stainless steels and nickel alloys to SSCC in elevated temperature H₂S-containing brines is related to:

- Alloy content
- The control of strength levels, and if these are reached by cold-working or heat treatment
- Control of the environment
- Galvanic interactions.

Stress cracking of these alloys has only been observed when the material was susceptible to pitting.

Figure 7 is frequently used as a guide for the selection of alloys for tubulars and other equipment in sweet and sour service. It is based on laboratory autoclave tests, usually done in the presence of 35,000 ppm chlorides, a pH of 4.0

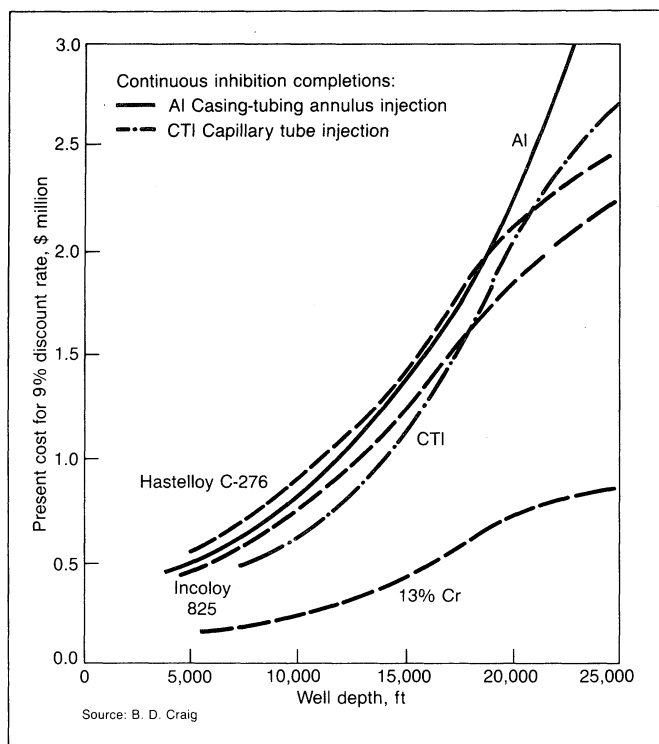


Fig. 8—Present cost of various completion schemes as a function of depth for discount rates of 9%.

and with 0.5 g/l of elemental sulfur. It would appear desirable to use Fig. 7 in combination with Fig. 6 to assure adequate resistance to pitting and to provide for the range of environmental conditions to which the tubulars will be exposed in their normal life cycle.

Example. Using Mobil's Mary Ann field as an example, from Fig. 7 we are inclined to believe that with 1,100 psi H₂S and 500 psi CO₂, Sanicro 28 may be adequate for the application. However, Fig. 6 shows us that with a pH of 3.5 to 4.0 under oxidizing free sulfur conditions (Scale A) and with 20,000 ppm chlorides and a temperature of over 400°F we can expect severe pitting on Alloy 28, and that C-276 or possibly Alloy 625 would be the correct selections. Pitting tendencies usually precede sulfide stress cracking. C-276 should also be selected for the packer and Alloy 625 for the cladding of the Christmas tree. These figures are intended as a quick screening guide only and tend to be conservative. There is no substitute for experience and evaluation in place.

The Fig. 6 curves have also proven to be helpful in determining alloys for CO₂ wells in EOR using either Scale B or C depending on temperature and H₂S content. Further, Fig. 6 Scale A can be used in the selection of stainless steels in seawater (pH 7.8) with the advisability to employ alloys with a pitting index of 38; this includes the 6% Mo stainless steels. Also the same philosophy can be applied to severe steamflooding and fireflood operations, and even in determining tubular and surface equipment requirements in geothermal operations and for brine disposal wells. Control of pH and working with a deaerated system is important in order to employ less expensive alloys.

Economic justification of CRA

Economic evaluations of projects have shown that the production rate (value of product) and operating/maintenance costs have the most significant effect, followed by capital cost. Many companies favor the use of corrosion inhibitors below 300°F. An economic study by Craig, shown in Fig. 8, indicates that the use of corrosion resisting alloys for various completion schemes becomes readily justifiable for depths over 17,000 feet for onshore installations. However, a case

can be made for offshore sour gas fields, where a CRA system can be justified for all depths based on the elimination of inhibitor treatment facilities, platform space and annual expense. This is summarized in Table 4. CRA's are generally more economical than chemically inhibiting steel tubing, except for shallow wells.

Outlook

The completion string of an oil or gas well is the heart of a production facility, and its safe and reliable operation is critical to the overall profitability of a field. Repairs to the completion system often run into millions of dollars. High-alloy stainless steels and nickel-base alloys offer great potential in revolutionizing well completion design by increasing allowable stress levels, removing inhibitor systems and basically making it possible to do operations not possible using conventional technology. Their role in frontier applications, such as offshore in deep water, in deep sour gas wells, in CO₂-enhanced oil recovery, in geothermal and in the Arctic, is becoming well established. Exchange of performance information of these alloys under aggressive, corrosive environments will be beneficial to all.

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