

SCF 19[®] Max Alloy:

A Materials Solution for Drilling in Aggressive Corrosion Environments

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ABSTRACT

Non-magnetic stainless steels are integral materials for modern drilling operations. They find usage throughout bottom-hole assemblies used for directional drilling. Their low magnetic permeability is critical for limiting drill string interference with magnetic sensing tools deployed near the drill bit. Corrosive environments within the most active drilling basins have grown increasingly hostile. Commonly utilized nitrogen-strengthened chrome-manganese steels have been pushed beyond their limits resulting in a dramatic reduction in tool longevity. This has principally been caused by two trends: the expanding usage of water-based chloride brines as drilling fluids in shale formations, and increasingly sour well conditions in the Middle East. Failures of non-magnetic stainless steels in these conditions are typically due to pitting, crevice corrosion, and stress corrosion cracking. The drilling industry needs an economical material with low magnetic permeability that satisfies the rigorous physical demands of the near-bit environment. Carpenter Technology proposes SCF 19 Max Alloy as a solution to this problem based on laboratory data and field experience.

REVIEW OF NON-MAGNETIC MATERIALS IN OIL AND GAS DRILLING

Operating companies need to know where their wells are going for a variety of reasons, not least of which is to maximize contact with the reservoir payzone. Magnetic survey tools are critical to directional drilling as they detect the azimuthal orientation of the bottom hole assembly (BHA). They function as a downhole compass near the drill bit, and enable wellbore trajectory control. Like a compass, azimuthal measurements can be fouled by interference from ferrous metals, particularly alloy steel drill pipe.

Therefore, non-magnetic drill collars (NMDCs) are integral components in modern directional drilling, as they minimize the distortion of the Earth's magnetic field at survey tools. The rapid growth in horizontal drilling since the mid-2000s (BHGE rig count) has increased utilization of NMDCs. However, their usage can be traced back to the 1930s in conjunction with the earliest downhole magnetic survey tools (Kopecki, 2010). The typical drill collar is approximately 30 feet long with an outer diameter between 4 and 9 inches.



Figure 1: Typical NMDCs in various diameters



Most BHAs used in directional drilling contain the following components: the drill bit, a mud motor or rotary-steerable unit, measuring-while-drilling (MWD) and/or logging-while-drilling (LWD) tools, NMDCs, stabilizers, and heavy-wall drill pipe. NMDCs perform the following functions in the BHA: apply weight on bit, provide buckling resistance, and serve as structural components for MWD/LWD tools (Collins, 2001). Drillers must analyze the components in the drill string, planned well trajectory, and the well's geographic location when determining the placement of non-magnetic materials within the BHA. Service companies compute required spacing of NMDCs above and below MWD/LWD tools based on the anticipated azimuth angle, wellbore inclination, and position of wellbore relative to the magnetic poles (Buchanan, 2013). Longer strings of NMDCs are required closer to the magnetic poles due to dip in the Earth's magnetic field.

Requirements for NMDC Alloys

Materials used in NMDCs have unique design requirements. They must have high strength, toughness, resistance to galling, corrosion resistance, and be non-magnetic. The most common alloys to date have been austenitic stainless steels of the nitrogen-strengthened chrome-manganese variety with yield strengths exceeding 140 ksi and toughness above 60 ft-lbs CVN. Fatigue life is a concern as horizontal drilling introduces alternating bending stresses as the drill string rotates. Most drill collars have a compressive bore treatment applied to the inner diameter to compensate for residual tensile stresses from warm-working and limit stress corrosion cracking (SCC). Additionally, alloys must be cost-effective.

History of NMDC Alloys

The first NMDC alloys were of the nickel-copper variety. These alloys have satisfactory corrosion resistance in chloride brines and superior galling resistance (Hondeborg, 1987). However, nickel-based alloys proved too expensive and were replaced by stainless steels in widespread use. Also, it is doubtful that these alloys could achieve the mechanical properties required by current specifications (Collins, 2001).

Chrome-nickel alloys were the first stainless steels used for drill collars and had formulations like 300 series stainless steels, typically 18 Cr, 8 Ni, 0.15 C (Collins, 2001). These alloys performed acceptably into the late 1970s, but proved to be susceptible to SCC. This was reported to have been due to elimination of chromate-based corrosion inhibitors for environmental reasons (Collins, 2001). Chrome-nickel alloys also have the additional disadvantage of reduced galling resistance compared to nickel-copper and chrome-manganese alloys.

The first generation of propriety chrome-manganese grades entered service in the 1960s, but without compressive bore treatments (Hondeborg, 1987). This left these collars vulnerable to SCC on the ID due to tensile residual stresses from the warm-working process (Kopecki, 2010). Cracks would often initiate in local corrosion pits on the bore, which served as stress risers. These alloys were used into the 1970s, but the introduction of water-based potassium and magnesium-chloride drilling muds caused the early chrome-manganese NMDCs to suffer unacceptable failure rates due to SCC (Hondeborg, 1987).

In the late 1970s, NAM, a division of Royal Dutch Shell, turned to 316L stainless steel as a stopgap for chrome-manganese stainless alloys that experienced a rash of failures in chloride muds. The 316L collars also suffered from SCC, but crack velocity and depth were sufficiently low that reconditioning could extend useful life (Hondeborg, 1987). Galling and the cost typical of chrome-nickel grades remained problematic.

The SCC issue in chrome-manganese grades was considerably improved by the commercial introduction of compressive bore treatments in 1983 (Kopecki, 2010). The operating envelope for chrome-manganese grades was expanded to include drilling fluids with higher chloride content. Chrome-manganese alloys were less expensive than chrome-nickel grades with superior galling resistance, and became commercial successes over the next 30 years.

Compressive bore treatments improved SCC resistance of chrome-manganese grades, but the problem was not eliminated. Grain boundary sensitization was also a significant cause of cracking into the early 1980s. Warm-working/forging practices required for strengthening can expose the material to temperatures that dwell around 1200 F. This can lead to precipitation of chromium-carbides and/or chromium nitrides at grain boundaries. The resulting chromium depletion in the surrounding grains leaves the area vulnerable to localized corrosion and cracking. Sensitization screening utilizing ASTM A262 was introduced in the early 1980s and mitigated sensitization as an issue for users (Collins, 2001).

This led to a chemistry refinement in chrome-manganese grades in which carbon was held as low as possible and essentially replaced with nitrogen (Collins, 2001). Grain boundary sensitization via chromium carbide formation during production was eliminated and nitrogen-strengthened chrome-manganese grades have been industry standards since the early 1990s. Incremental improvements in chemistry, melting, and forging continued; leading to higher strength and corrosion resistance with each iteration.



SCF® 19 (20 Cr, 18 Ni, 5 Mn, 5 Mo) was first introduced in the 1980s. The alloy's composition rendered it impervious to the most common corrosive environments of the time, but it's introduction coincided with bore-treated chrome-manganese grades which rendered it commercially unattractive. However, increasingly aggressive environments associated with horizontal drilling in shale reservoirs have led to problems with pitting corrosion and SCC in chrome-manganese grades. This issue is acute in tight spaces like seal bores and thread roots, where no compressive surface treatment exists. Therefore, chrome nickel grades like SCF 19 Max Alloy have increased in popularity with drillers contending with these conditions.

Shale Reservoirs

Horizontal drilling of shale formations combined with hydraulic fracturing have unlocked huge oil and gas reserves previously considered unrecoverable. Shales are fine-grained, sedimentary rocks composed of clays and other minerals with low permeability. They are the most abundant sedimentary rock and can include relatively large amounts of organic material relative to other rock types (Oilfield glossary). The clays in shales swell when contacted by fresh water due to osmosis. Highly saline water is trapped within the shale's pores and fresh water will migrate to regions of higher salinity. This effect can work to move fluid into or out of the reservoir depending on the salinity of the water phase within the wellbore. Consequently, the pore pressure within the reservoir will increase or decrease. Increasing pore pressure due to osmosis into the formation can cause the shale to fail and create an unstable wellbore (Zoback, 2007).

Furthermore, clays are chemically reactive due to cation exchange. K*, Na*, Mg**, and Ca**, are loosely bound to negatively charged sites within the clay. Cations vary in their compatibility with negatively charged sites, so exchange is possible (Breeden, 2004). Ion exchange will occur with ionically bonded chlorides in drilling mud like KCl and CaCl2. Hydration of exchangeable cations also contributes to clay swelling, though this effect is much slower than osmotic swelling (Lal, 1999). Ion exchange continually reduces the effectiveness of the drilling fluid to inhibit swelling and additional cations must be added during drilling (Oilfield glossary).

Drilling Fluids

Drilling fluids are the critical link between the drill string and the reservoir during drilling operations. Their design is critical to drilling a successful well. Drilling fluids are designed to serve several key functions. Chief among them is to provide hydrostatic pressure to maintain well control while drilling. Other functions include suspending and transporting cuttings, supplying hydraulic power to the drill bit, lubricating the drill string, and minimizing wellbore damage. Drilling fluids come in many varieties (Petrowiki), including pneumatic systems utilizing compressed air. However, the most common drilling fluids can be generally characterized as being either oil-based or water-based.

Oil-based muds were developed in the 1960s to handle difficult drilling conditions and are formulated with diesel, mineral oil, or low-toxicity linear olefins and paraffins. The olefins and paraffins are commonly known as "synthetics" as they can be synthesized from smaller molecules (Petrowiki). Oil-based fluids are ideally suited to inhibit shale swelling and were traditionally employed in these situations. However, oil based fluids have several detractors, including their cost and environmental impact concerns. Transportation, cuttings removal, and disposal are complex relative to water-based systems.

TABLE 1: Mud weights achievable with various brines	
Brine Type	Mud Weight
Potassium Formate	8.4-13.1 lbm/gal
Potassium Chloride	8.3-9.7 lbm/gal
Sodium Chloride	8.3-10.0 lbm/gal
Sodium Bromide	8.4-12.5 lbm/gal
Calcium Chloride (CaCl ₂)	8.4-11.8 lbm/gal
Calcium Bromide (CaBr ₂)	8.4-14.2 lbm/gal
CaCl ₂ /CaBr ₂ mix	11.8-15.2 lbm/gal
CaCl ₂ /CaBr ₂ /Zinc Bromide (ZnBr ₂) mix	14.2-19.2 lbm/gal
ZnBr ₂	14.2-19.2 lbm/gal
Cesium Formate	15.0-19.2 lbm/gal

The compositions of individual oil-based fluids are intricate, but broadly exist as either inverted brine emulsions, commonly known as inverts, or all-oil systems. Typically, barite is added for density, bentonite as a viscosifier, surfactants for oil-wetting invert emulsions, and lime for pH control (Petrowiki). Emulsified brines typically have oil/water ratios between 70/30 and 90/10. Calcium chloride brine is the most common because it appears to have the best shale inhibition properties (Petrowiki). Alternatively, all-oil systems with diesel or synthetic bases and no water phase can be employed in long shales laterals with variable reservoir salinity (Petrowiki). Diesel muds have long been an industry mainstay for drilling in shales.



Water-based muds are used in most wells because of their cost advantage over oil-based fluids (Petrowiki). The base fluid may be fresh water, seawater, brine, saturated brine, or a formate brine. Saltwater muds are used to inhibit shale swelling and solids-free or low-solids systems can be formulated from heavy brines. Table 1 shows mud density ranges achievable with brine systems, the selection of which will depend on reservoir properties (Carpenter, 2017).

Polymer drilling fluids are a type of water-based mud that are used for reactive formations with significant requirements for shale inhibition (Petrowiki). Polymers like xanthan gum are used to provide the viscosity profile necessary to transport cuttings instead of bentonite, while potassium chloride is most often the brine base due to its effectiveness and low cost (Petrowiki). Potassium ions participate in clay ion exchange and are effective swelling inhibitors. Glycol and amine-based inhibitors can also be used in polymer fluids.

Changes in Drilling Conditions and NMDCs

The "Shale Revolution" that has occurred in North America in the past decade is arguably the most significant development in the history of the oil and gas industry. The process of drilling horizontal wells into shale formations followed by hydraulic fracturing has unlocked resources previously considered unrecoverable. Oil production in the United States exceeded 10 million barrels per day in 2018 for the first time since the 1970s (U.S. EIA) thanks to these unconventional resources. This change in drilling practices had a profound effect on the environment in which NMDCs must perform, as the exposure time between shale formations and wellbores during drilling has dramatically increased.

Water-based Brine Muds in North America

Conventional wells could manage shale swelling without significant increases in brine concentration by utilizing mud weights, mud additives, well trajectory control, and minimal time in contact with shales (Lal, 1999). As the contact time in horizontal wellbores is significantly higher, changes in drilling fluid compositions were required. Cost advantages, environmental concerns with oil-based muds, and shale inhibiting properties of brines have caused water-based fluid systems to increase in popularity as horizontal drilling into shale formations has proliferated in North America.

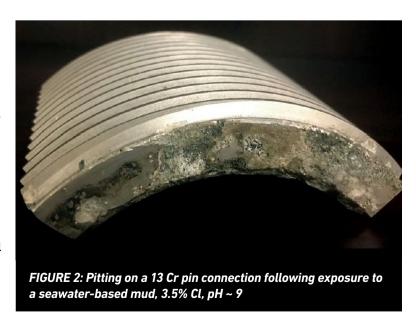
Calcium chloride has become a preferred brine for water-based systems in shale reservoirs because it can achieve moderate fluid weights and is an effective shale inhibitor. Bromides can also be added to weight up the mud in higher pressure zones. Whereas earlier drilling fluids, particularly inverts, relied on solids for weighting, these heavy brines double as both swelling inhibitors and densifiers. The mud weights achievable in water-based brines are limited by the solubility limits of the salt.

As with other alkaline earth metals, calcium is hygroscopic, meaning it tends to attract and hold water. Therefore, these muds tend to stick to collars as clumps after they are pulled from the hole and racked back. These wet clumps provide the electrolyte to form aggressive corrosion cells that intensify as the mud clumps dry and local salinity increases. The situation can be made worse if the mud has an acidic pH and reduced alkalinity due to service.

Effect of Brines on NMDCs

Experience has shown that pitting is the most common reason modern NMDCs are removed from service. SCC is also an issue when operating in chloride brines at elevated temperature, but increasing pitting resistance tends to also reduce susceptibility to SCC. Pitting occurs most aggressively in confined regions on the collar's inner diameter, typically threads and seal bores. These happen to be the most critical machined features of NMDCs and recuts are required if pits develop in these areas. Many expensive tools, like MWD and LWD tools, can only tolerate a limited number of cutbacks on the NMDC before the tool must be scrapped. Pits can also form on the outer surface, but it is not uncommon to continue using collars until they are significantly deep.

An example of pitting corrosion on a 13-chrome stainless alloy is shown in Figure 2. Here, pits





formed on the pin's thread nose, which was exposed to a seawater-based mud inside the drill string. The chloride content of seawater muds is approximately 3.5%, which is nearly 10 times less than brine-weighted muds used in shales. Buffering agents are usually added to seawater muds to hold the pH around 9. The thread flanks were protected from pitting by the pipe dope.

Corrosion during storage is reportedly the most significant cause of pitting damage on NMDCs and thus appears to be the most pressing issue facing North American users. The matter is complicated by operations in locations with limited access to fresh water for cleaning, as is the case in arid climates and offshore. Resistance to pitting and crevice corrosion at ambient storage temperatures is the critical design criterion for alloys evaluated for this problem. The most popular chrome-manganese grades currently in service are now being stretched up to, and beyond, the limits of their performance. Outdoor storage in hot climates, which can cause material temperatures to reach near 80 °C in direct sunlight, can easily exceed the critical pitting temperatures of these grades.

NMDCs in Sour Service

In addition to the drastic shift in drilling activity in North America, conditions in other major fields have also become more aggressive. Hydrogen sulfide has long been an issue in Saudi Arabia, particularly for sour gas production from the Khuff formation (Oilfield glossary). The Tengiz field in Kazakhstan is another major oil producer with significant sour gas content. Sour gas is so abundant that the operator utilizes sour gas injection to recycle the H₂S for reservoir stimulation (Chevron, 2008). As these reservoirs deplete, H₂S production tends to increase, making drilling conditions for new wells more hostile.

Drill strings are exposed to $\rm H_2S$ when drilling in sour formations due to sour gas entering drilling fluids via cuttings. The primary failure in NMDCs associated with sour service is sulfide stress cracking, which typically occurs in box threads. These longitudinal cracks don't usually lead to downhole failures, but major recuts of threads will be required to return the asset to service. Stainless steel alloys with improved corrosion resistance will be less susceptible to cracking as they will limit hydrogen sulfide from being reduced to atomic hydrogen, which causes hydrogen embrittlement.

Carbonate Formations

The downhole corrosion environment can also be affected by remedial activities performed to fix formation damage. Drilling in carbonate formations does not in itself place special demands on materials. However, there are cases when hydrochloric acid treatments are used to clear blockages that might form due to formation damage during drilling. Amine corrosion inhibitors are typically used in conjunction with the acid to protect the carbon steel drill string. Unfortunately, these inhibitors are ineffective on stainless steels. The current generation of chrome-manganese alloys are susceptible to damage. It is believed that more resistant chrome-nickel alloys would mitigate this problem.

Requirements for NMDC Material Solutions

The arrival of increasingly aggressive conditions brought on by drilling long laterals in shale formations coincided with the largest oil price collapse since the early 1980s. Therefore, material solutions for NMDCs must not only have improved corrosion performance, but also reduce the total cost of ownership. Lifecycle costs associated with NMDCs include raw material, machining, recuts and repair, and scrapping tool assemblies that can include expensive electronics. Extending the lifetime of non-magnetic components, especially those that are integrated with electronics and other critical components, can provide a tremendous savings.



SCF 19® MAX ALLOY AS A SOLUTION

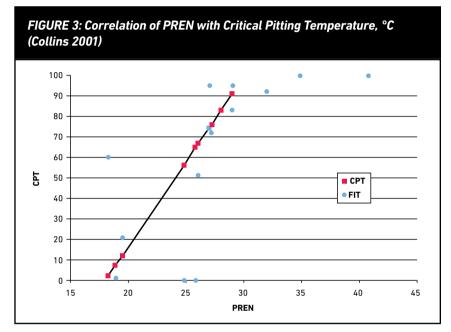
SCF 19 $^{\circ}$ Max alloy is a chrome-nickel-molybdenum stainless steel alloy with a nominal chemical composition of 20Cr, 18Ni, 5Mn, 5Mo. This chemistry gives the alloy a modified pitting resistance equivalence number (PREN_{mod}) of 40 compared to a PREN_{mod} of 28 for SCF 260 $^{\circ}$ alloy, Carpenter Technology's most pitting-resistant chrome-manganese grade. These PRENs were computed with the modified equation (1) below which accounts for the deleterious effect of manganese (Collins, 2001).

PRENmod = Cr(wt %) + 3.3 x Mo(wt %) + 16 x N(wt %) - 0.5 x Mn(wt %)

(1)

PREN calculations for NMDC alloys, even when unmodified for manganese content, have proven to correlate with pitting resistance. Figure 3 shows a plot of critical pitting temperatures in a 1M brine at — 0.1 V_{SCE} plotted against PREN using equation (1) with the Mn term omitted. The alloys tested were chrome-manganese stainless steels with chromium contents ranging from 13% to 27% (Collins, 2001). The 13-chrome grades proved to have inferior performance, particularly those with relatively higher carbon contents. Critical pitting temperatures in these cases were sometimes less than 5 °C. the cutoff for a valid test (Collins, 2001).

Lab testing has demonstrated superior corrosion performance of chrome-nickel-moylbdenum grades over nitrogen-strengthened chrome-manganese grades in boiling magnesium chloride and calcium chloride (Holzleitner, 2007), confirming the general indications given by the modified PREN.



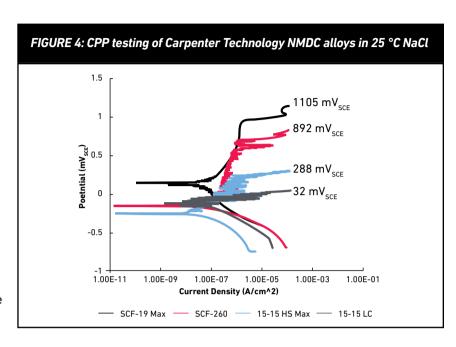
The first version of SCF 19 alloy was developed by Carpenter Technology in the 1980s, but did not find commercial success because its introduction coincided with cheaper bore-treated chrome-manganese grades that solved most SCC problems at the time. However, early field trials demonstrated superior corrosion resistance in potassium-magnesium-chloride brines (Hondeborg, 1987). It has been Carpenter Technology's longstanding belief that SCF 19 Max alloy is the optimum solution for aggressive drilling brines.



Corrosion Testing

Critical pitting potential (CPP) and critical pitting temperature (CPT) testing were done on SCF 19® Max alloy to quantify its performance relative to chrome-manganese grades (Kernion, 2017). These tests were conducted in sodium chloride brines and compared the performance of SCF 19 Max alloy with Carpenter Technology's nitrogenstrengthened chrome-manganese grade alloys: SCF 260®, 15-15 HS®Max, and 15-15 LC® Mod.

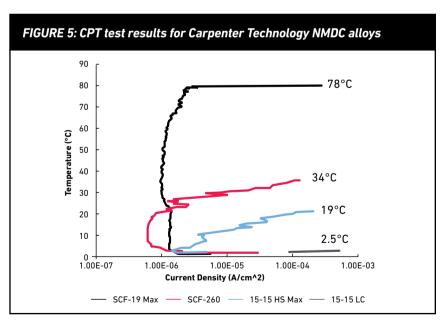
Figure 4 shows the results of CPP testing conducted in an 8% sodium chloride solution at 25 °C. The pitting potential of SCF 19 Max alloy, at 1105 mV, was shown to be superior to all chrome-manganese grades tested. This agrees with the superior corrosion resistance of SCF 19 Max alloy that has been reported in field trials both in North America and the Middle East.



Critical pitting temperature is also a key indicator of alloy performance in corrosive brines. This parameter is particularly important when failures are caused by pitting during storage in warm climates. An alloy whose CPT exceeds the temperature of the chloride media to which it is exposed will not suffer pitting damage. Carpenter Technology's NMDC alloys were tested to determine their CPTs per the ASTM G150 standard in a 1 M NaCl solution. Samples were held at a potential of $0.7~V_{\text{SCE}}$ and temperature was increased at 1 °C/min until the corrosion current reached 100 μ A/cm². Results are shown in Figure 5.

The data in Figure 5 showed a CPT of 78 °C for SCF 19 Max alloy, more than 30°C higher than the best performing nitrogenstrengthened chrome-manganese grade, SCF 260 alloy. This confirms SCF 19 Max alloy holds substantial promise for mitigating pitting corrosion during storage.

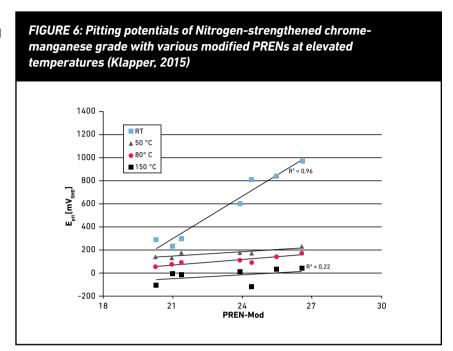
The more difficult issue to address is the performance of NMDCs at elevated temperatures in chlorides. Recent work on nitrogen-strengthened chrome-manganese grades has confirmed the pitting potentials of these alloys tend to become both lower and less differentiated based on modified PREN as temperatures approach downhole conditions (Klapper, 2015). A plot of this effect in an 80,000 ppm chloride solution is shown in Figure 6.





The data in Figure 6 suggests that downhole performance of stainless NMDC alloys related to SCC is a much stronger function of surface residual stresses than pitting potential. Compressive residual stresses exist on both collar inner and outer diameters thanks to compressive bore treatments and residual forging stresses, respectively.

Field history from users is critical to determining the weighting given to downhole SCC mitigation versus pitting damage during storage and transport. If data shows that bore-treated collars are sufficiently resistant to SCC, then attention could be turned toward the pitting and crevice corrosion issue. To solve the latter problem, critical pitting temperature could be utilized as a requirement for NMDC stainless steel alloys. Carpenter Technology's experience with the NMDC rental fleet of Amega West Services, a Carpenter Technology, suggests that



upgrading to SCF 19® Max alloy to address pitting has increased NMDC life without adverse SCC effects. Similar resistance to cracking has also been noted by users in sour service.

Mechanical Properties

SCF 19 Max alloy can meet the properties required for use as NMDCs. The alloy is available with 140 ksi minimum yield stress in bar sizes up to 8.5 inches. Development work is currently underway to extend this yield strength to larger sizes. SCF 19 Max alloy also displays excellent toughness, with typical Charpy V-notch (CVN) values exceeding 150 ft-lbs. Carpenter Technology's internal minimum is 100 ft-lbs CVN. Fatigue life has been acceptable during field usage and fatigue testing is done routinely at the mill as a process check.

Galling resistance of chrome-nickel grades has been a prevailing concern within the industry since their introduction (Hondeborg, 1987). However, Carpenter Technology's experience indicates that properly treated threads can be made up to the drill collar torque values specified in API 7-1 without galling. Shot peening and bead blasting threads combined with an effective pipe dope can mitigate this issue. Dopes containing calcium fluoride have proven particularly effective.

As with other Carpenter Technology NMDC grades, a proprietary compressive treatment is applied to the bores of SCF 19 Max collars. This treatment applies a superior depth of compressive stress relative to other processes like roller burnishing and hammer peening. It has proven highly effective in preventing SCC originating on collar IDs in multiple alloys.



CONCLUSIONS

The NMDC materials, reservoir conditions, and drilling fluids have been reviewed to provide context and highlight the magnitude of changes that have occurred because of the North American energy revolution and subsequent price pressure on operators. The key takeaways are the following:

- NMDCs are critical components of drill strings for directional drilling and must meet a unique and challenging set of requirements.
- Horizontal drilling in shale formations has required increasing use of water-based brine drilling fluids weighted with chlorides which have created more aggressive corrosion environments.
- Field experience suggests that in North America most collars are now removed from service due to pitting corrosion, likely due to a lack of cleaning before transportation and storage.
- The industry should consider using critical pitting temperature as the key requirement for using the current generation of NMDC alloys in brines.
- An economical replacement for popular chrome-manganese NMDC alloys with superior corrosion resistance and acceptable mechanical properties is required.
- Sour service conditions in the Middle East and other large fields are becoming more hostile and require upgraded alloys to prevent cracking.
- Carpenter Technology's SCF 19® Max alloy is an ideal candidate for extending NMDC life and reducing total costs due to repairs and scrapped tools. The alloy has superior corrosion resistance, acceptable mechanical properties, and an effective price point.
- SCF 19® Max alloy should be considered by NMDC users operating in hostile corrosive environments including brines and sour service.



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