High Performance Age-Hardenable Nickel Alloys Solve Problems in Sour Oil and Gas Service

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INTRODUCTION

The new frontier of oil and gas exploration will be with deep wells, particularly in deepwater. Most of the "easy-to-pick" fruit have been taken with shallow field development. Compared to shallow wells, deep wells generally require more high-performance, nickel-base alloys. Wells are categorized as being either "sweet" or "sour." Sweet wells are only mildly corrosive, while sour wells are very corrosive. Sour wells can contain hydrogen sulfide, carbon dioxide, chlorides, and free sulfur. There are different levels of corrosive conditions that are compounded by temperatures up to 500°F (260°C) and pressures up to 25,000 psi (172 MPa). Deep wells generally have higher temperatures and pressures. Material selection is especially critical for sour gas wells. The materials of choice must be corrosion-resistant, cost-effective, reliable, and have the required strength for the well conditions. As these conditions become more severe, material selection changes from carbon steels for "sweet" wells, to duplex (austenitic-ferritic) stainless steel, to INCOLOY® alloys 825 or 925™, to INCONEL® alloys 725HS and 725™ for sour well service. The limiting chemical compositions of the nickel-base alloys are displayed in Table 1.

Table 1. Limiting Chemical Composition (Weight %) of Nickel-Base Alloys.

Alloy (UNS No.)	Ni	Cr	Mo	Cu	Co	Al	Ti	Fe	Other
INCONEL alloy C-276 (N10276)	Balance	14.5–16.5	15.0 – 17.0	-	2.5 max	-	-	4.0–7.0	W, 3.0 – 4.5
INCONEL alloy 718 (N07718)	50.0–55.0	17.0–21.0	2.80 – 3.30	-		0.2 – 0.8	0.65 – 1.15	Bal.	Nb, 4.75 – 5.50
INCONEL alloys 725 & 725HS (N07725)	55.0–59.0	19.0–22.5	7.0 – 9.5	-	-	0.35 max.	1.00 – 1.70	Bal.	Nb, 2.75 – 4.0
MONEL alloy K-500 (N05500)	63.0–70.0	-	-	Bal.	-	2.03 – 3.15	0.35 – 0.85	2.00 max.	-
INCOLOY alloy 825 (N08825)	38.0-46.0	19.5-23.5	2.5-3.5	1.5-3.0	-	0.2 max	0.6-1.2	22.0 min	
INCOLOY alloy 925 (N09925)	42.0–46.0	19.5–22.5	2.5 – 3.5	1.5 – 3.0	-	0.10 – 0.50	1.90 – 2.40	22.0 min	Nb, 0.50 max

Materials have to meet criteria for corrosion resistance and mechanical properties in service environments needing increased reliability for the lifetime of the exploited asset. Age-hardened nickel-base alloys and cold-worked solid solution nickel-base alloys offer many advantages such as

high-strength, toughness, low magnetic permeability and excellent corrosion resistance. The choice of material for a particular set of well conditions is based on a number of selection criteria including:

- Mechanical properties
- General corrosion resistance
- Pitting & crevice corrosion resistance
- Chloride stress corrosion cracking resistance
- Sulfide stress corrosion cracking resistance

MATERIAL SELECTION PROPERTIES

Mechanical Properties

The strength levels of age-hardened materials are increasing in importance, particularly for offshore applications exploiting high-pressure deep well reserves, where weight considerations can affect the economic viability of a project. Material selection for down-hole and wellhead equipment such as hangers, sub-surface safety valves, pumps and packers require age-hardenable alloys to obtain the necessary strength in heavier cross-sections which cannot be strengthened by cold work. Nickel alloys commonly used for these applications include INCOLOY alloy 925, MONEL alloy K-500, and INCONEL alloys 718, X-750, 725, and 725HS. Typical mechanical properties of high-performance nickel alloys used in oil country applications are shown in Table 2.

Table 2. Typical Room Temperature Mechanical Properties.

Alloy UNS No.	Material Condition	Yield Strength		Tensile Strength		% El.	Hardness
		ksi	MPa	ksi	MPa		
MONEL alloy 400 N04400	Annealed	31.3	216	78.6	542	52	60 HRB
	Cold Worked	93.7	646	108.8	716	19	20 HRC
INCONEL alloy 625 N06625	Annealed	69.5	479	140.0	965	54	95 HRB
	Cold Worked	125.7	867	150.4	1037	30	33 HRC
INCONEL alloy 718 N07718	Solution Annealed & Aged	134.0	924	191.5	1320	20	39 HRC
INCONEL alloy 725/725HS N07725	Alloy 725, Solution Annealed & Aged	132.9	916	183.3	1264	28	36 HRC
	Alloy 725HS, Annealed & Aged	151.3	1043	199.4	1375	25	42 HRC
	Alloy 725, Solution Annealed plus Cold Worked & Aged	163.3	1126	189.6	1307	15	38 HRC
INCONEL alloy X-750 N07750	Aged	132.8	916	188.0	1296	27	34 HRC
INCOLOY alloy 825 N08825	Annealed	47.0	324	100.0	690	45	85 HRB
	Cold Worked	114.0	786	130.5	900	15	28 HRC
INCOLOY alloy 925 N09925	Solution Annealed & Aged	113.0	779	176.0	1214	26	36 HRC
	Cold Worked	129.0	889	140.0	965	17	32 HRC
	Cold Worked & Aged	153.0	1055	176.0	1214	19	---
	Cast, Solution Annealed & Aged	106.7	736	127.5	879	23	29
INCONEL alloy C-276 N10276	Annealed	52.0	359	110.4	761	64	83 HRB
	Cold Worked	156.9	1082	172.5	1189	17	35 HRC

* The values shown represent typical strength levels.

The age-hardened alloys are used at different strength levels depending on the application. Generally INCOLOY alloy 925 is used at a 758 MPa (110 ksi) minimum yield strength level. The minimum yield strength level for INCONEL alloys 718 and 725 is 827 MPa (120 ksi). INCONEL alloy 725HS is used at a 965 MPa (140 ksi) minimum yield strength level. The enhanced strength properties of INCONEL alloy 725HS have been achieved through optimized thermal and mechanical processing.

Galvanic Compatibility

Galvanic corrosion can be a concern when dissimilar materials are in contact in a conductive fluid. The INCOLOY and INCONEL alloys are generally noble and consideration is given towards the system design when in contact with less noble materials. In galvanic compatibility tests performed in ambient temperature seawater for 92 days at LaQue Center for Corrosion Technology, INCONEL alloys 725 and 625 were determined to be galvanically compatible. Coupling a large surface of INCONEL alloy 725 to MONEL alloy K-500 promoted corrosion of the alloy K-500 component.

General Pitting and Crevice Corrosion Resistance

Traditionally, corrosion-resistant alloys are screened first by their pitting resistance equivalent number (PREN), and then by the equivalent cracking data generated in sour brine environments[1]. Equation 1 shows a typical formula used to compare the pitting resistance of stainless steels and nickel-base alloys.

$$\text{PREN} = \%\text{Cr} + 1.5(\%\text{Mo} + \%\text{W} + \%\text{Nb}) + (30 \times \%\text{N}) \qquad \text{Equation 1}$$

The critical pitting temperature (CPT) for an alloy is determined by exposing samples in acidified 6% ferric chloride solutions, according to ASTM Standard Test Method G48, Method C [2], and raising the temperature by incremental amounts until the onset of pitting. New unexposed test specimens and fresh ferric chloride solution are used at each test temperature. The tests are only valid up to 85°C because at higher temperatures the test solution becomes unstable. The minimum accepted CPT for an alloy is 40°C for many offshore applications (e.g., the North Sea). A ranking of alloys is shown in Table 3.

Table 3. CCT and CPT for Alloys Tested per ASTM G48.

Alloy	CCT (°C)	CPT (°C)	PREN
INCONEL alloy 686	>85	>85	51
INCONEL alloy C-276	45	>85	45
INCONEL alloy 725	35	>85	41
INCONEL alloy 625	30 – 35	≥85	41
INCOLOY alloy 25-6MO	30 - 35	65 – 70	36
Duplex stainless steel 2205	20	30	31
INCOLOY alloy 825	5	30	26
316 Stainless Steel	<0	15	21

Determining the critical crevice temperature (CCT) of an alloy involves exposing samples to the same aggressive test solution but with a multiple crevice device (TFE-fluorocarbon washer) attached to the surface of the test specimen. The temperatures shown in Table 3 indicate the onset of crevice corrosion.

Resistance of Age Hardened Nickel-Base Alloys to Corrosion by Seawater.

Nickel alloys with a PREN greater than 40 are very resistant to crevice corrosion in natural seawater service. Table 4 compares the crevice corrosion resistance of corrosion-resistant alloys in seawater. Under both stagnant and flowing conditions, the weight losses are extremely low.

Table 4. Effect of PREN* on Crevice Corrosion Resistance in Seawater

Alloy	% Mo	PREN*	Crevice Test	Exposure Days	Max. depth of attack mm
INCONEL alloy 718	3.0	22.5	Washers	30	0.41
INCOLOY alloy 825	3.2	26	Washers	30	0.25
INCOLOY alloy 25-6MO	6.5	36	Vinyl Sleeve	60	0.13
INCONEL alloy 625	9	41	MCA	90	0
INCONEL alloy 725	9	41	Washers	30	0
INCONEL alloy 686	16	51	PCA	60	0

Vinyl Sleeve – very tight crevice formed on OD of a tube sample.
MCA – surface ground finish, with Delrin crevice assemblies.
PCA – surface ground and pickled with Perspex crevice assemblies.
*Equation 1

Table 5 shows crevice corrosion test results for INCONEL alloys 625 and 725 using more severe crevice geometry. Alloy 725 exhibited excellent corrosion performance and showed no attack, while the alloy 625 samples crevice corroded during the test to a maximum depth of 0.66 mm. The titanium content in INCONEL alloy 725 appears to have a beneficial effect in improving crevice corrosion resistance in seawater.

Table 5. Crevice Corrosion Resistance* of INCONEL® alloys 625 and 725,

Alloy	Observed Initiation days	Percent of sites attacked	Maximum Depth of attack (mm)
INCONEL alloy 625	2 to 5	25 to 75	0.02 to 0.66
INCONEL alloy 725	None at 30 days	0	0.00

*evaluated in quiescent seawater at 30°C for 30 days, using acrylic plastic crevice devices torqued to 25 in-lbs (0.288 m-kg).

Resistance to General Corrosion in Sour Environments

In mineral acids[3], INCONEL alloy 725 in the age-hardened condition has comparable corrosion resistance to INCONEL alloy 625. Good general corrosion resistance can be important in resisting the various chemicals injected as inhibitors and dispersants.

Weight loss tests in hydrogen sulfide environments are shown in Table 6. INCONEL alloy 625 and INCOLOY alloy 925 show good resistance to general corrosion in this test environment and marginally higher performance than INCONEL alloy 718.

Table 6. Weight Loss Tests in Hydrogen Sulfide Environments.

Alloy	H_2S Pressure (kPa)	Corrosion Rate (mm/year)	
		149 °C	204 °C
INCONEL alloy 625	69	0.000	0.003
	345	0.008	0.010
	690	0.003	0.005
INCOLOY alloy 925	69	0.003	0.003
	345	0.010	0.013
	690	0.003	0.010
INCONEL alloy 718	69	0.076	0.008
	345	0.018	0.058

	690	0.003	0.030
9Cr/1Mo Steel	69	-	-
	345	5.23	7.06
	690	7.59	4.37

Note: Autoclave tests were 14 days in 15% NaCl/distilled water with total gas pressure of 6.9MPa consisting of 3.4MPa CO_2 plus N_2 with H_2S at partial pressures between 69 and 690kPa.

Environmental Cracking

Wellhead and downhole components must resist stress corrosion cracking (SCC). The potential for SCC becomes greater with higher temperature and higher concentration of H_2S and the presence of chloride ions and elemental sulfur. Lower temperature hydrogen embrittlement and sulfide stress cracking (SSC) are also potential failure mechanisms which may be promoted by galvanic corrosion, acidic conditions, and dissolved H_2S.

Resistance to Sulfide Stress Cracking and Hydrogen Embrittlement

In general, resistance to SCC, SSC, and hydrogen embrittlement increases with increasing content of nickel, chromium, molybdenum, tungsten and niobium in an alloy.

Table 7 shows hydrogen embrittlement tests conducted on duplicate specimens of the alloy 725HS in accordance with Test Level III of NACE TM-0177[4]. C-ring specimens were galvanically coupled to steel. A minimum test duration of 720 hours is required by the specification. In this case, the heat-treated alloy 725HS specimens surpassed this test limit and there was no cracking in the sour brine environment, while cold worked alloy 625 exhibited cracking after 10 days.

Table 7. Sulfide Stress Cracking and Hydrogen Embrittlement Resistance*

Alloy	0.2% YS ksi	0.2% YS Mpa	HRc	Test Duration Hours	Cracking Yes : No
INCONEL alloy 725HS	160	1102	43	>720	No: No
INCONEL alloy 725	129	888	40	>720	No: No
INCONEL alloy 718	130	896	34	>720	No: No
INCONEL alloy 625 (Cold Worked)	160	1103	38	240	Yes
INCOLOY alloy 925	114	786	38	>1000	No

*Steel Coupled C-Rings per NACE TM 0177, 25% NaCl + 0.5% Acetic Acid + H_2S Saturated at 25°C.

Stress Corrosion Cracking

Alloy strength is a factor in environmental cracking susceptibility. Materials become more prone to environmental cracking as their strength increases. In order to obtain the optimum level of strength, ductility and toughness, and cracking resistance, maximum hardness levels are specified for each alloy in NACE International's Materials Requirement MR0175[5] (see Table 8).

Table 8. NACE MR0175 Maximum Hardness for Sour Service.

UNS No.	Condition	HRC Maximum
N05500	Hot Worked and Age-Hardened, Solution-Annealed, Solution-Annealed and Aged-Hardened	35
N06625	All	35
N06686	Annealed and Cold-Worked	40

N07718	Solution-Annealed, Hot Worked, Hot Worked and Aged	35
	Solution-Annealed and Aged	40
N07725	Solution Annealed and Aged	40
	Annealed and Aged	43
N09925	Solution-Annealed	35
	Solution-Annealed and Aged	38
N10276	Cold-Worked and Unaged for Service Over 250°F (121°C)	45

H. R. Copson [6] originally reported the beneficial effect of alloy nickel content on chloride SCC resistance of austenitic type alloys in 1959. Alloys 825, 925, 718, 625 and 725 all contain 42% or greater nickel and, as a result, are all very resistant to stress corrosion cracking in water containing chlorides.

Stress corrosion cracking test results for C-ring test pieces in a simulated sour well environment containing free sulfur are shown in Table 9. INCONEL alloy 725 exhibited good resistance to SCC in the presence of elemental sulfur up to 232°C, while INCONEL alloy 718 cracked at 135°C and cold worked INCONEL alloy 625 cracked at 191°C.

Table 9. C-Ring Test Results*

Alloy	Yield Strength		Test Temperature (°C) Cracking (Yes/No)					
	Ksi	MPa	135	177	191	218	232	246
INCONEL alloy 725	129	887	-	No:No	No:No	No:No	Yes:No	
INCONEL alloy 725	133	917	-	No:No	No:No	No:No	No:No	Yes:No
INCONEL alloy 718	130	898	Yes:Yes					
INCONEL alloy 625 Cold worked	144	992	-	No	Yes			
INCONEL alloy 625 Cold worked	160	1102	-	No	Yes			

* 100% Yield Strength in 25% NaCl plus 0.5% Acetic Acid plus 1g/L Sulfur plus 0.827MPa H_2S for 14 Days.

A more severe test in ranking materials performance is the slow strain rate (SSR) test. Common pass/fail criteria for SSR testing is a ratio of time to failure (TTF), % reduction of area (%RA) and % elongation (%El) measured in a simulated oil patch environment relative to the same parameter in an inert environment (gases such as air or nitrogen). These are referred to as "critical ratios". TTF, %RA and %El ratios of ≥0.80 typically represent passing behavior in SSR tests. If the ratios are below 0.90, the specimen is examined under a scanning electron microscope for evidence of ductile or brittle fracture on the primary fracture surface. Tests exhibiting ductile behavior are acceptable while those with brittle fracture are not. All specimens are examined for secondary cracking in the gage length away from the primary fracture. The absence of secondary cracking is indicative of good SCC or SSR resistance and passes. The presence of secondary cracks is cause for rejection. One or more inert (air) SSR tests are conducted along with two or more environmental SSR tests for each test lot of material [7]. The decision to use the critical ratio of ≥0.80 as the acceptance criterion in SSR tests was based upon results obtained earlier for cold worked solid solution nickel-base alloys [8,9]. Studies [10] have shown that INCOLOY alloy 925 is consistently more crack resistant in severe Mobile Bay type sour brine environments than alloy 718, based on SSR stress corrosion cracking data. Table 10 shows a summary of the performance of alloy

725HS in the NACE SSR test TM0198, in the level VI environment of 20% NaCl, 3.5Mpa H_2S, 3.5Mpa CO_2 at 175° C.

Table 10. Performance of alloy 725HS in NACE Test Level VI.

Alloy	Yield Strength		HRc	SSR Ratio		Comments
	Ksi	MPa		Elongation Ratio	RA Ratio	
INCONEL alloy 725HS	149 – 160	1027 - 1102	43	0.96 - 1.16	0.82-0.97	No failures Normal Ductile Behavior No indication of secondary cracking

SUMMARY

Ultimately, it is the user's responsibility to establish the acceptability of an alloy for a specific oilfield environment. The data presented here should be helpful in selecting materials for the corrosive environments of sour oilfields. A group of alloys that represents a range of alternatives can be selected for testing in an environment simulating the oilfield environment under study. A final material selection for a specific application should be made based on test results and an economic analysis of cost-effective alternatives.

INCONEL alloy 725 offers resistance to corrosion in extremely sour brine environments and in the presence of elemental sulfur at temperatures up to 242°C. The maximum permitted hardness under NACE MR0175 requirements is 40 HRc. The stress corrosion cracking resistance of age-hardened INCONEL alloy 725 is superior to that of INCONEL alloy 718 in sour environments.

A high-strength grade of alloy 725, INCONEL alloy 725HS, has been assigned a NACE MR0175 maximum hardness level of 43 HRc and can be used for high-strength applications in sour service up to NACE test level VI at 175°C.

The corrosion resistance of age-hardened nickel-base alloys in sour brine environments is as follows[11]:

INCONEL alloy 725> INCONEL alloy 725HS > INCOLOY alloy 925 > INCONEL alloy 718 > MONEL alloy K-500 and INCONEL alloy X-750

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