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

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In the coming years the new frontier of oil and gas exploration will be in deep wells, and particularly those in deepwater. Most of the easy to pick fruits of the industry have already been taken with shallow field development. Compared to shallow wells, deep wells generally require equipment built with more high performance nickel base alloys. Wells are categorized either being sweet or sour. Sweet wells being only mildly corrosive, while sour wells are highly corrosive and contain hydrogen sulfide, carbon dioxide, chlorides and free sulphur. In addition different levels of corrosive conditions are compounded by temperatures up to 260Deg C and pressures up to 25,000psi and generally 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 nickel based alloys such as Incoloy® alloys 825 and 925, Inconel® alloys 725HS and 725. The limiting chemical compositions of the nickel based alloys are displayed in Table 1.

Table 1 : Limiting Chemical Composition of Nickel based Alloys (Weight %)

Alloy (UNS No)	Ni	Cr	Mo	Cu	Co	Al	Ti	Fe	Other
Inconel® C276 (N10276)	Bal	14.5-16.5	15.0 - 17.0	-	2.5 max	-	-	4.0-7.0	W3.0-4.5
Inconel® 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® 725 + 725 HS (N07725)	50.0 - 59.0	19.0 - 22.5	7.0 - 9.5	-	-	0.35 max	1.0 - 1.70	Bal	Nb 2.75 - 4.0
Monel® K 500 (N05500)	63.0 - 70.0	-	-	Bal	-	2.03 - 3.15	0.35 - 0.85	2.00 max	-
Incoloy® 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® 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

Table 1 : Limiting Chemical Composition of Nickel based Alloys (Weight %)
Materials need to meet criteria for corrosion resistance and mechanical properties in service environments requiring increased reliability for the lifetime of the well. Age hardened nickel based alloys and cold worked solid worked nickel based 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 and crevice corrosion resistance
- Chloride stress corrosion cracking resistance
- Sulfide stress corrosion cracking resistance

Materials Selection 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 call for age hardenable alloys in order 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® 925, Monel® K500 and Inconel® 718, X750, 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	Yeild Strength Ksi	Yeild Strength Mpa	Tensile Strength Ksi	Tensile Strength Mpa	% Elong	Hardness
Monel® 400	Annealed	31.3	216	78.6	542	52	60 HRB
(N04400)	Cold Worked	93.7	646	108.8	716	19	20 HRC
Inconel® 625	Annealed	69.5	479	140.0	965	54	95 HRB
(N06625)	Cold Worked	125.7	867	150.4	1037	30	33 HRC
Inconel® 718 (N07718)	Solution Annealed + Aged	134.0	924	191.5	1320	20	39 HRC
Inconel 725+725HS (N07725)	Alloy 725 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, Cold Worked + Aged	163.3	1126	189.6	1307	15	38 HRC
Inconel® X750 (N07750)	Aged	132.8	916	188.0	1296	27	34 HRC
Incoloy® 825	Annealed	47	324	100	690	45	85 HRC
(N08825)	Cold Worked	114	786	130.5	900	15	28 HRC
Incoloy® 925 (N09925)	Solution Annealed + Aged	113	779	176	1214	26	36 HRC
	Cold Worked	129	889	140	965	17	32 HRC
	Cold Worked + Aged	153	1055	176	1214 -	19	
	Cast, Solution Annealed + Aged	106.7	736	127.5	879	23	29
Inconel® C276	Annealed	52	359	110.4	761	64	83 HRB
(N10276)	Cold Worked	156.9	1082	172.5	1189	17	35 HRC

The age hardened alloys are used at different strength levels depending on the application. Generally Incoloy® 925 is used at 758 Mpa (110 Ksi) min yield strength level. The min yield strength level for Inconel® 718 and 725 is 827 Mps (120 Ksi). Inconel® 725HS is used at a 965 Mpa (140 Ksi) min yield strength level. The enhanced strength properties of Inconel® 725HS have been achieved through optimized thermal and mechanical processing.

Galvanic Compatibilty

Galvanic corrosion is caused when dissimilar materials are in contact in a conductive fluid. The Incoloy® and Inconel® alloys are generally noble materials. In galvanic compatibility tests performed in ambient temperature seawater for 92 days at LaQue Centre for Corrosion Technology. Inconel® 725 and 625 were determined to be galvanically compatible. Coupling a large surface of Inconel® 725 to Monel® K500, promoted corrosion of the alloy K500 component.

General Pitting and Crevice Corrosion

Traditionally corrosion resistant alloys are graded first by their pitting resistance equivalent number (PREN) and then by the equivalent cracking data generated in sour brine environment. Equation 1 shows a typical formula used to compare the pitting resistance of stainless steels and nickel based alloys.

$$PREN = \%Cr + 1.5(\%mo+\%W+\%Nb)+30+\%N) \quad \textbf{Equation 1}$$

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 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 85Deg C because at higher temperatures the test solution becomes unstable. The minimum accepted CPT for an alloy is 40 Deg C for many offshore applications (eg North Sea). A ranking of alloys is shown in Table 3.

Table 3 CCT and CPT for Allots tested to ASTM G48

Alloy	CCT Deg C	CPT Deg C	PREN
Inconel® 686	>85	>85	51
Inconel® C276	45	>85	45
Inconel® 725	35	>85	41
Inconel® 625	30 – 35	> 85	41
Incoloy® 25-6 Mo	30 – 35	65 – 70	36
Duplex stainless steel 2205	20	30	31
Incoloy® 825	5	30	26
316 stainless steel	<0	15	21

Determining the critical temperature (CCT) of an alloy involves exposing samples to the same aggressive test solution but with a multiple crevice device (TFE-flourocarbon 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 based 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 Resistant in Seawater.

Alloy	% Mo	PREN	Crevice Test	Exposure Days	Max depth of attack mm
Inconel® 718	3.0	22.5	Washers	30	0.41
Incoloy® 825	3.2	26	Washers	30	0.25
Incoloy® 25 -6Mo	6.5	36	Vinyl Sleeve	60	0.13
Inconel® 625	9	41	MCA	90	0
Inconel® 725	9	41	Washers	30	0
Inconel® 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® 625 and 725 using more severe crevice geometry. Inconel® 725 displays excellent corrosion performance and showed no attack, while the alloy 625 samples corroded during the test to a maximum depth of 0.66mm. The titanium content in Inconel® 725 has a beneficial effect in improving crevice corrosion resistance in seawater.

Table 5 Crevice Corrosion Resistance of Inconel® 725 and 625

Alloy (UNS No)	Observed Initiation days	Percentage of sites attacked	Max Depth of attack (mm)
Inconel® 625	2 – 5	25 – 75	0.02 to 0.66
Inconel® 725	None at 30 days	0	0.00

General Corrosion in Sour Environments

In mineral acids Inconel® 725 in the age hardened condition has comparable corrosion resistance in Inconel® 625. The use of various chemicals injected as inhibitors and dispersants means that good general corrosion resistance is also required in sour wells.

Weight loss tests in hydrogen sulphide environments are shown in Table 6. Inconel® 625 and Incoloy® 925 show good resistance to general corrosion in the test environment and marginally higher performance than Inconel® 718.

Table 6: Weight Loss Tests in Hydrogen Sulphide Environments

Alloy	H2S Pressure (Kpa)	Corrosion Rate 149Deg C	204Deg C
Inconel® 625	69 345 690	0.000 0.008 0.003	0.003 0.010 0.005
Inconel® 925	69 345 690	0.003 0.010 0.003	0.003 0.013 0.010
Inconel® 718	69 345 690	0.076 0.018 0.003	0.008 0.058 0.030
9Cr/1 Mo Steel	69 345 690	- 5.23 7.59	- 7.06 4.37

Note: Autoclave tests were 14 days in 15% Na/Cl.distilled water with total gas pressure of 6.9Mpa consisting of 3.4Mpa Co2 pus N2 with H2S partial pressures between 69 and 690 Kpa.

Environmental Cracking

It is imperative that wellhead and downhole components resist stress corrosion cracking (SCC). The potential for SCC becomes greater with higher temperature and higher concentration of H2S and the presence of chloride ions and elemental sulphur.

Potential failure in service can also be caused by lower temperature hydrogen embrittlement and sulphide stress cracking (SSC). These conditions may be accelerated by galvanic corrosion coupled with acidic conditions and dissolved H2S.

Suphide Stress Cracking and Hydrogen Embrittlement

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

Table 7 shows hydrogen embtrittlement tests conducted on duplicate specimens of the Inconel® 725HS in accordance with Test Level III of NACE TM-0177. 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 Inconel® 725HS specimens surpassed this test limit and there was no cracking in the sour brine environment, while cold worked Inconel® 625 exhibited cracking after 10 days.

Table 7 Sulphide Stress Cracking and Hydrogen Embrittlement Resistance

Alloy	0.2% VS Ksi Mpa	HRe	Test Duration Hours	Cracking Yes:No
Inconel® 725HS	160 1102	43	>720	No:No
Inconel® 725	129 888	40	>720	No:No
Inconel® 718	130 896	34	>720	No:No
Inconel® 625 Cold Worked	160 1103	38	240	Yes
Incoloy® 825	114 786	38	>1000	No

*Steel coupled C Rings per NACE TM-0177 25%NaCl+0.5%Acetic Acid + H2S Saturated at 25 Deg C.

Stress Corrosion Cracking

The strength of an alloy is a governing factor in its resistance to 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 the maximum hardness levels are specified for each alloy in NACE International Materials Requirements MR0175 (see Table 8).

Table 8 NACE MR0175 Maximum Hardness for Sour Service

UNS no	Condition	HRC Max
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 121 Deg C	45

HR Copson originally reported the beneficial effect of alloy nickel content on chloride SCC resistance of austenitic type alloys in 1959. Alloys 825, 925, 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 sulphur are shown in Table 9 Inconel® 725 exhibited good resistance to SCC in the presence of elemental sulphur up to 232 Deg C while Inconel® 718 cracked at 135 Deg C and cold worked Inconel® 625 cracked at 191 Deg C.

Table 9 C Ring Test Results

Alloy	Yield Strength		Test Temperature (Deg C) Cracking (Yes/No)					
	Ksi	Mpa	135	177	191	218	232	246
Inconel® 725	129	887	-	No:No	No:No	No:No	Yes:No	
Inconel® 725	133	917	-	No:No	No:No	No:No	No:No	Yes:No
Inconel® 718 Cold Worked	130	89	Yes:Yes					
Inconel® 625 Cold Worked	144	992	-	No	Yes			
Inconel® 615 Cold Worked	160	1102	-	No	Yes			

*100% Yield Strength in 25% NaCl plus 0.5% Acetic Acid plus Lg/L Sulphur plus 0.827Mpa H_2S for 14 days.

A more severe test in ranking the performance of materials 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 processing 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 are usually accepted as pass rates in SSR tests.

If the ratios are below 0.90 the specimen is examined under a scanning electron microscope for the evidence of ductile or brittle 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. The decision to use the critical ratio of >0.80 as the acceptance criterion in SSR tests was based upon results obtained from earlier tests on cold worked solid solution nickel-base alloys.

Studies have shown that Incoloy® 925 is consistently more crack resistant in severe Mobile Bay type sour brine environments than Inconel® 718. This conclusion is based on SSR stress corrosion cracking data. Table 10 shows a summary of the performance of Inconel® 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 Deg C.

Table 10 Performance of Inconel® 725HS in NACE Test Level IV

Alloy	Yield Strength		HRe	SSR Ratio		Comments
	Ksi	Mpa		Elongation Ratio	RA Ratio	
Inconel® 725HS	149 - 160	1027 - 1102	43	0.96 – 1.16	0.82 – 0.97	No failures. Normal Ductile behaviour. No indication of secondary cracking.

Summary

Ultimately it is the users’ responsibility to establish the acceptability a specific material for use in an oilfield environment. The data presented her is designed to help in selecting materials for the corrosive environments of sour oilfields. A final material selection for a specific application should be made based on test results and an economic analysis of cost effective alternatives.

Inconel® 725 offers resistance to corrosion in extremely sour brine environments and in the presence of elemental sulphur of temperature up to 242 Deg C. The maximum permitted hardness under NACE MR 0175 requirements is 40 HRC. The stress corrosion cracking resistance of age hardened Inconel® 725 is superior to that of Inconel® 718 in sour environments.

A high strength grade of Inconel® 725 and Inconel® 725HS has been assigned a NACE MR0175 maximum hardness level of 43 HRC and can be used for high strength application in sour service up to NACE test level VI at 175 Deg C.

The corrosion resistance of age hardened nickel based alloys in sour brine environments is as follows-

Inconel® 725 > Inconel® 725HS > Incoloy® 925 > Inconel® 718 > Monel® K 500 > Inconel® X750 > Inconel® 625

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